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# THE UNITED STATES OF AMERICA

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UNITED STATES DEPARTMENT OF COMMERCE

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*April 12, 2005*

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APPLICATION NUMBER: 60/550,167

FILING DATE: *March 04, 2004*

RELATED PCT APPLICATION NUMBER: PCT/US05/06379



Certified by

*Don W. Dudas*

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Practitioner's Docket No.

**TAS-6969PV**

**PATENT**

Preliminary Classification:

Proposed Class:

Subclass:

Note: "All applicants are requested to include a preliminary classification on newly filed patent applications. The preliminary classification, preferably class and subclass designations, should be identified in the upper right-hand corner of the letter of transmittal accompanying the application papers, for example 'Proposed Class 2, subclass 129.'" M.P.E.P. § 601, 7<sup>th</sup> ed.

**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of: **William E. Eckles and Thorsten Kuehler**

For: **AMINE-BASED POLYMERS**

**Mail Stop Provisional Patent Application**

**Commissioner for Patents**

**P.O. Box 1450**

**Alexandria, VA 22313-1450**

**COVER SHEET FOR FILING PROVISIONAL APPLICATION**  
**(37 C.F.R. § 1.51(c)(1))**

**WARNING:** "A provisional application must also include the cover sheet required by § 1.51(c)(1) or a cover letter identifying the application as a provisional application. Otherwise, the application will be treated as an application filed under paragraph (b) [nonprovisional application] of this section." 37 C.F.R. § 1.53(c)(1). See also M.P.E.P. § 201.04(b), 6th ed., rev. 3.

**EXPRESS MAILING UNDER 37 CFR § 1.10\***

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I hereby certify that this paper, along with any document referred to, is being deposited with the United States Postal Service on this date March 4, 2004, in an envelope addressed to the Mail Stop Provisional Patent Application, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450, as "Express Mail Post Office to Addressee" Mailing Label No. EU-712715410US.

Date: March 4, 2004

Anita J. Galo

*(type or print name of person certifying)*

*Anita J. Galo*  
Signature of person certifying

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NOTE: "A complete provisional application does not require claims since no examination on the merits will be given to a provisional application. However, provisional applications may be filed with one or more claims as part of the application. Nevertheless, no additional claim fee or multiple dependent claims fee will be required in a provisional application." Notice of December 5, 1994, 59 Fed. Reg. 63,951, at 63,953. "Any claim filed with a provisional application will, of course, be considered part of the original provisional application disclosure." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

NOTE: "A provisional application is not entitled to the right of priority under 35 U.S.C. 119 or 365(a) or § 1.55, or to the benefit of an earlier filing date under 35 U.S.C. 120, 121 or 365(c) or § 1.78 of any other application. No claim for priority under § 1.78(a)(3) may be made in a design application based on a provisional application. No request under § 1.293 for a statutory invention registration may be filed in a provisional application. The requirements of §§ 1.821 through 1.825 regarding application disclosures containing nucleotide and/or amino acid sequences are not mandatory for provisional applications." 37 C.F.R. § 1.53(c)(3).

NOTE: "No information disclosure statement may be filed in a provisional application." 37 C.F.R. § 1.51(d). "Any information disclosure statements filed in a provisional application would either be returned or disposed of at the convenience of the Office." Notice of December 5, 1994, 59 Fed. Reg. 63,591, at 63,594.

NOTE: "No amendment other than to make the provisional application comply with the patent statute and all applicable regulations may be made to the provisional application after the filing date of the provisional application." 37 C.F.R. § 1.53(c).

NOTE: 35 U.S.C. 119(e)(1) requires that a nonprovisional application be filed within twelve months of the filing date of the provisional application for the nonprovisional application to claim the benefit of the filing date of the provisional application. Under 35 U.S.C. 21(b) and 119(a)(3), if this twelve-month period expires on a non-business day, it is extended to expire on the next business day.

This is a request for filing a **PROVISIONAL APPLICATION FOR PATENT** under 37 C.F.R. § 1.51(c)(1)(i).

1. The following comprises the information required by 37 C.F.R. § 1.51(c)(1):
2. The name(s) of the inventor(s) is/are (37 C.F.R. § 1.51(c)(1)(ii):

NOTE: "If the correct inventor or inventors are not named on filing a provisional application without a cover sheet under § 1.51(c)(1), the later submission of a cover sheet under § 1.51(c)(1) during the pendency of the application will act to correct the earlier identification of inventorship." 37 C.F.R. § 1.48(f)(2).

NOTE: "The naming of inventors for obtaining a filing date for a provisional application is the same as for other applications. A provisional application filed with the inventors identified as 'Jones et al.' will not be accorded a filing date earlier than the date upon which the name of each inventor is supplied unless a petition with the fee set forth in § 1.17(i) is filed which sets forth the reasons the delay in supplying the names should be excused. Administrative oversight is an acceptable reason. It should be noted that for a 35 U.S.C. 111(a) application to be entitled to claim the benefit of the filing date of a provisional application the 35 U.S.C. 111(a)(1) application must have at least one inventor in common with the provisional application." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,209.

The term "invention" is typically used to refer to subject matter which applicant is claiming in his/her application. Because claims are not required in a provisional application, it would not be appropriate to reference joint inventors as those who have made a contribution to the "invention" disclosed in the provisional application. If the "invention" has not been determined in the provisional application because no claims have been presented, then the name(s) of those person(s) who have made a contribution to the subject matter disclosed in the provisional application should be submitted. Section 1.45(c) states that "if multiple inventors are named in a provisional application, each named inventor must have made a contribution, individually or jointly, to the subject matter disclosed in the provisional application." All that § 1.45(c) requires is that if someone is named as an inventor, that person must have made a contribution to the subject matter disclosed in the provisional application. When applicant has determined what the invention is by the filing of the 35 U.S.C. 111(a) application, that is the time when the correct inventors must be named. The 35 U.S.C. 111(a) application must have an inventor in common with the provisional application in order for the 35 U.S.C. 111(a) application to be entitled to claim the benefit of the provisional application under 35 U.S.C. 119(e). Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,208.

See 37 C.F.R. § 1.53.

1.	<u>WILLIAM</u> GIVEN NAME	<u>E.</u> MIDDLE INITIAL OR NAME	<u>ECKLES</u> FAMILY (OR LAST) NAME
2.	<u>THORSTEN</u> GIVEN NAME	<u></u> MIDDLE INITIAL OR NAME	<u>KUEHLER</u> FAMILY (OR LAST) NAME
3.	<u></u> GIVEN NAME	<u></u> MIDDLE INITIAL OR NAME	<u></u> FAMILY (OR LAST) NAME

3. Residence address(es) of the inventor(s), as numbered above (37 C.F.R. § 1.51(c)(1)(iii)):

1. 2603 PRINCETON ROAD, CLEVELAND HEIGHTS, OH-44118
2. WESTERFELDSTRASSE 50h, D-33611 BIELEFELD, GERMANY
3.

4. The title of the invention is (37 C.F.R. § 1.51(c)(1)(iv)):

AMINE-BASED POLYMERS

5. The name, registration, customer and telephone numbers of the practitioner (if applicable is (37 C.F.R. § 1.51(c)(1)(v)):

Name of practitioner: RICHARD A. SUTKUS

Reg. No.: 43,941

Tel. (216) 621-2234

Customer No. 26,294

*(complete the following, if applicable)*

☐ A power of attorney accompanies this cover sheet.

6. The docket number used to identify this application is (37 C.F.R. § 1.51(c)(1)(vi)):  
Docket No.: TAS-6969PV

7. The correspondence address for this application is (37 C.F.R. § 1.51(c)(1)(vii)):

**TAROLLI, SUNDHEIM, COVELL & TUMMINO L.L.P.**  
**526 SUPERIOR AVENUE, SUITE 1111**  
**CLEVELAND, OH 44114-1400**

8. Statement as to whether invention was made by an agency of the U.S. Government or under contract with an agency of the U.S. Government. (37 C.F.R. § 1.51(c)(1)(viii)).

This invention was made by an agency of the U.S. Government, or under contract with an agency of the U.S. Government.

☒ No.

☐ Yes.

The name of the U.S. Government agency and the Government contract number are: \_\_\_\_\_

9. Identification of documents accompanying this cover sheet.

A. Documents required by 37 C.F.R. §§ 1.51(c)(2)-(3):

Specification:	No. of pages	<u>FORTY (41)</u>
Drawings:	No. of sheets	<u>( ) (Figs. - )</u>

B. Additional documents:

<input checked="" type="checkbox"/> Claims:	No. of claims	<u>EIGHT (8) (ONE (1) Page)</u>
<input type="checkbox"/> Abstract:	No. of pages	<u></u>

Note: See 37 C.F.R. § 1.51.

- ☐ Power of attorney
- ☐ Small entity assertion
- ☐ Assignment
- ☐ English language translation of non-English provisional application

NOTE: A provisional application which is filed in a language other than English, does not have to have an English language translation. See 37 C.F.R. § 1.52(d)(2). However, if the provisional application is not in the English language and will later serve as a benefit of its filing date for a nonprovisional application, other than a design patent, or for an international application designating the U.S., then an English language translation must be filed in the provisional application or the later filed nonprovisional application. See § 1.78(a)(5)(iv).

- ☐ This application is in a language other than English and an English translation along with a statement of its accuracy is submitted herewith.
- ☐ Other

10. Fee

The filing fee for this provisional application, as set in 37 C.F.R. § 1.16(k), is \$160.00, for other than small entity, and \$80.00, for a small entity.

- ☒ Applicant is a small entity.

NOTE: "A . . . statement in compliance with existing § 1.27 is required to be filed in each provisional application in which it is desired to pay reduced fees." Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,197.

11. Small entity statement assertion

- ☐ The assertion that this is a filing by a small entity under 37 C.F.R. § 1.27 (c)(1) is attached ("ASSERTION OF SMALL ENTITY STATUS").
- ☒ Small entity status is asserted for this application by payment of the small entity filing fee under § 1.16(k). 37 C.F.R. § 1.27(c)(3).

12. Fee payment

- ☒ Fee payment in the amount of \$80.00 is being made at this time.
- ☐ No filing fee is to be paid at this time (This and the surcharge required by 37 C.F.R. § 1.16(l) can be paid subsequently).

13. Method of fee payment

- ☒ Attached is a ☒ check ☐ money order in the amount of \$80.00
- ☒ Authorization is hereby made to charge the amount of \$0.00
- ☒ to Deposit Account No. 20-090
- ☐ to Credit card as shown on the attached credit card information authorization form PTO-2038.

**WARNING:** Credit card information should not be included on this form as it may become public.

- ☒ Charge any additional fees required by this paper or credit any overpayment in the manner authorized above.

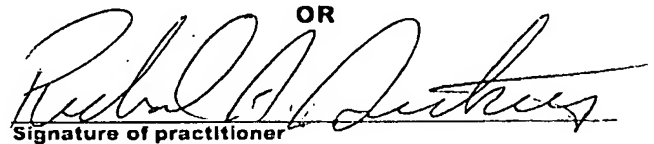
A duplicate of this paper is attached.

Date: \_\_\_\_\_

\_\_\_\_\_  
Signature of submitter

Tel.: \_\_\_\_\_

Date: March 4, 2004

OR  
  
Signature of practitioner

Reg. No. 43,941

RICHARD A. SUTKUS

(type or print name of practitioner)

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PROVISIONAL APPLICATION

"Express Mail" Mailing Label Number

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March 4, 2004

DATE OF DEPOSIT

Anita J. Galo

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Anita J. Galo

NAME OF PERSON SIGNING

03/04/2004

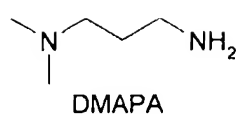
DATE OF SIGNATURE

AMINE-BASED POLYMERS

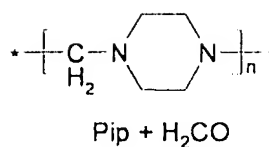
The following materials and claims provide description(s), etc of the present invention.



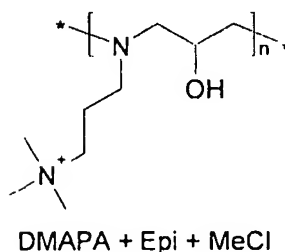
1) DMAPA + Epi



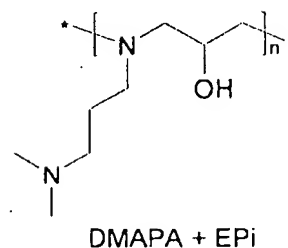
2) DMAPA + Epi + MeCl



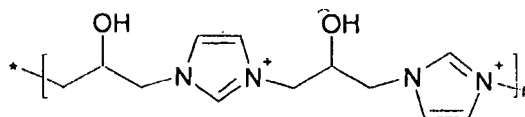
3) Pip + Epi

4) Pip + H<sub>2</sub>CO + Epi

5) IMZ + Epi



6) Mirapol



The first three examples describe reaction products of Epi with different amines. They have in common that a polymer is formed during the reaction which give rise to grain refined zinc deposits from alkaline electrolytes. In case of the quaternised polymer

also a brightening effect is observed. Example 4 shows the case of a crosslinked polymer that also yields bright deposits. Example 5 shows that not only aliphatic and alicyclic but also aromatic amines may be used.

The available literature and the filed patents since the late 50's show that the field of Epi reaction products was subject to intense scrutineering by many scientists and an enormous variety of combinations of amines has already been tested.

The latest "new" development in the field of intermediates for alkaline zinc plating was the introduction of Mirapol and its derivatives.

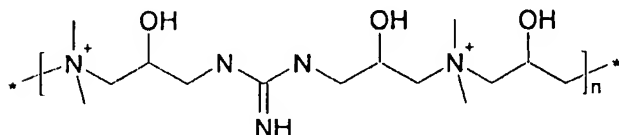
Bill Eckles presented some recent results that he had obtained in this field. According to this a polymer that contains a guanidino instead of a urea functionality gives rise to a virtually identical brightness and levelling as the original material.

It was concluded, that three different fields are available that might give rise to new improved intermediates: 1) "simple" Epi-amin reaction products, 2) Mirapol-like derivatives, 3) new intermediates of different structure (?).

During the discussion it was pointed out that the chances of finding something new in field 1) are not very good, due to the enormous amount of work that has already been done! A possible way to extract new results based on this chemistry might nevertheless lie in finding new structural motives.

#### Experiments:

To get a better general understanding of this chemistry a look into field 1) is surely interesting and therefore we decided to react Epi with Guanidin Carbonate and Dimethylamin:



The target molecule shown above contains a guanidino unit and quaternised amino groups. According to Bill a polymer of Dimethylamin and Epi provides grain refinement over a large current density area. The combination of the two functionalities as described above might therefore yield grain refining plus brightening!?

The reactions are performed in a 1 L three necked flask with magnetic stirrer, dropping funnel, internal thermometer and condenser.

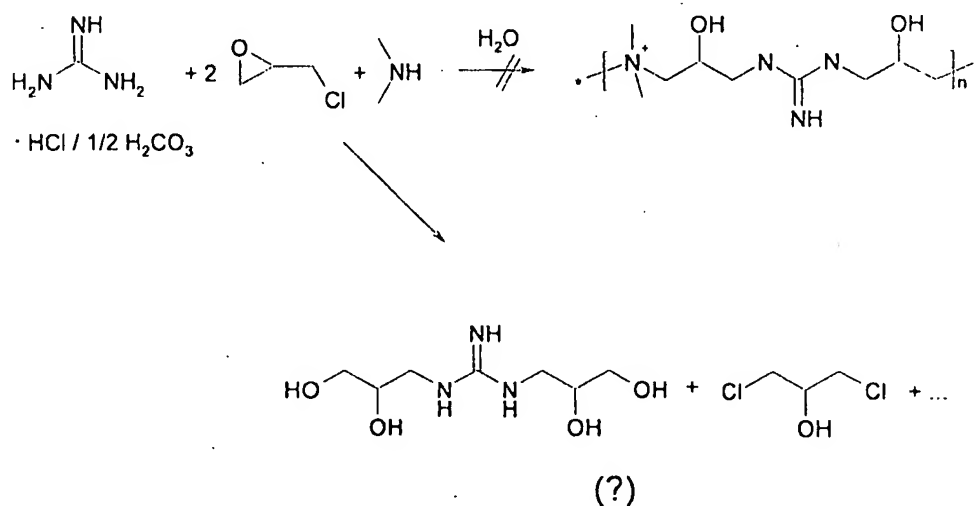
In a first trial Guanidine carbonate (GC) was dissolved in 250 mL of water (pH 11.5) and the solution heated to 60°C. After that 90 g of Epi were added within five minutes. After heating to 80°C a gas evolution was observed and the temperature rose to 95°C within the next 30 minutes. A clear colourless solution was obtained. Following this 55 g of a 40% solution of Dimethylamin were added in 10 minutes. The mixture was heated to reflux at 101°C for 2 ½ h. The now yellow solution was cooled to room temperature (pH 8.8). The solution exhibited a strong smell of unreacted Dimethylamin (→ TKT 1-5).

To determine the potential of the product as a brightener a Hull cell test was performed. 1 mL of the mixture was added to a Hull cell containing a solution of 11.5 g/L Zn, 1 mL Xenithe ANC WC (EDTA soln.) and 0.2 mL Xenithe ANC Purifier (thiourea soln.) A Hull cell panel was plated for 5 min. at 3 A.

The resulting deposit was grey, dull and dendritic over the whole cd range.

Another 45 g Epi was added to the reaction mixture and refluxed for 1 ½ h. The product was now slightly lighter in colour. No smell of amin was detected but the sample smelled more of halogenated hydrocarbons.

The product was tested in the Hull cell according to the procedure described above. Again a dull, grey and dendritic deposit was obtained.

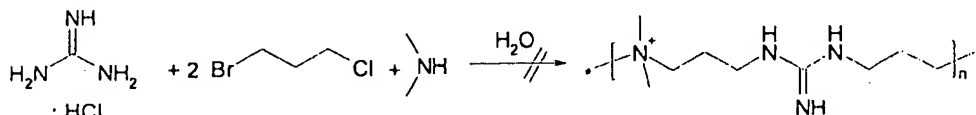


To product was analysed by IR spectroscopy. The spectrum showed signals for the Guanidino functionality as well as a pattern that might be attributed to a glycol functionality.

Taking into account all available data it was concluded that probably the reaction of the Epi with guanidin was incomplete and the Epi was in large parts hydrolysed or reacted with HCl from hydrolysis of intermediates. The major part of the dimethylamine is probably driven out of the reaction mixture without reacting at all. The degree of hydrolysis might be due to the high pH of the starting solution. To start with a solution of lower pH the same reaction was repeated with Guanidin hydrochloride (pH 5.2). The resulting product mixture showed similar properties ( $\rightarrow$  TKT 1-7). Again no grain refining or brightening effect could be observed in the Hull cell test.

Based on these results it was decided to substitute the Epi by trimethylen chlorobromide (TMCB) to have a reagent that is less sensitive to hydrolysis. The experimental set-up was the same as described above.

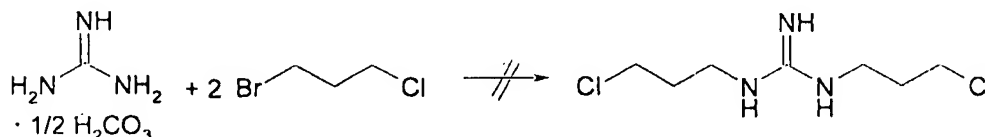
47 g of Guanidin hydrochloride were dissolved in 250 mL of water and the pH adjusted to 9.7 by adding 5 g of Sodium carbonate. The solution was heated to 64 °C and 151 g (95 mL) of trimethylen chlorobromide were added within 20 minutes. During the addition the temperature rose to 85°C and two liquid phases formed in the reaction flask. After 1 h at 85 °C the pH had fallen to 8 and the solution was allowed to cool down to 68 °C. 55 g of a 40% solution of dimethylamin were added within 10 minutes. The mixture was stirred for 10 minutes and hen heated to reflux at 94 °C for 2 h. After cooling to room temperature the two phases are separated. The lower phase (V = 55 mL) consists of trimethylenchlorobromide. The reaction can not be completed ( $\rightarrow$  TKT 1-9).



The fact that no complete reaction can be obtained is probably due to the imiscibility of the trimethylenchlorobromide with the aqueous phase. The product was not tested for possible brightening properties.

From the previously described results it was concluded that reactions of Guanidin with difunctional electrophiles like Epi or trimethylen chlorobromide are subject to limitations and side reactions whenever water is present in relevant amounts. To avoid interference it was decided to react Guanidin carbonate with trimethylene chlorobromide without solvent.

The components (22 g GC and 76 g TMCB) were heated in a one necked flask with condenser and magnetic stirring. To control the reaction the temperature of the vapour phase above the reaction mixture was measured. The mixture was refluxed for 3 ½ h. The temperature during this time never exceeded 102 °C which is probably due to water formed during the reaction (b.p. trimethylen chlorobromide 140 °C!). During refluxing the mixture changed from one liquid and one solid phase to two liquid phases. After this 10 g of Na<sub>2</sub>CO<sub>3</sub> was added to the mixture to neutralise hydrobromic acid that is possibly formed during the reaction and afterwards the mixture was refluxed for another 3h. After cooling to room temperature the lower phase became solid. The residue was filtered off and washed with 150 mL diethyl ether.



The product was a very hygroscopic colourless solid (→ TKT 1-10). The IR spectrum allowed no definite identification of the residue as the desired product. One possible interpretation of the results obtained is that instead of a electrophilic attack of the TMCB at the amino nitrogen only an exchange of the carbonate ion for a bromide ion is observed. No further steps were undertaken to verify this hypothesis.

#### Preliminary Conclusions:

The results described above lead to the following conclusions:

The nucleophilicity of Guanidin seemingly is not pronounced enough to allow reaction with Epi or TMCB easily.

Due to this fact, reactions of this type under aqueous conditions often lead to hydrolysis of the electrophile.

Phase separations (liquid/liquid, liquid/solid) tend to aggravate the problems.

A possible way to facilitate the formation of the desired products might be the use of organic solvents.

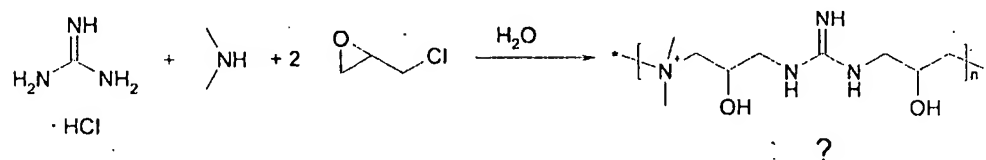
Could a stricter control of the reaction conditions (pH, Temperature, ...) yield a passable route to the desired product?

#### Outlook:

On the background of these findings it was decided to focus on I) changing reaction conditions to possibly obtain the desired molecule, II) other monomers and maybe III) variations on the Mirapol motive.

Considering the fact that reaction products that contain guanidin in the formulations are currently in use, it must be taken into account that it is possibly the reaction conditions that have a strong influence on the reactivity of guanidin with Epi. An additional experiment was performed to further examine this influence.

In a three necked flask with dropping funnel, internal thermometer, condenser and magnetic stirring 47 g (0.48 mol) of guanidin hydrochloride (GHC) and 55 g / 62 mL (0.48 mol) of 40 % dimethylamin (DMA) were dissolved in 250 mL of water. The mixture was heated to 45 °C and 95 g / 80 mL of Epi were added dropwise so that the temperature stayed below 55 °C for most of the time during the addition. The clear homogeneous reaction mixture was stirred for 15 min and then heated to reflux for 3 h (→ TKT 1-15).



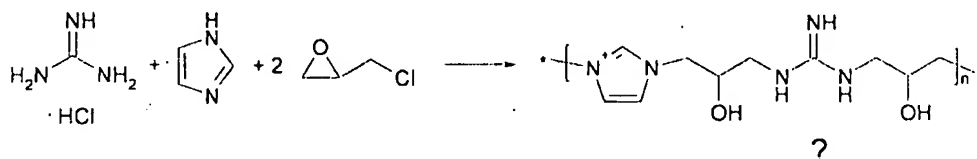
A sample of the solution was dried by evaporating excess water and an IR-spectrum was obtained of the residual viscous oil. The spectrum matched the one obtained from the reaction done before in which first the Epi was added to the guanidin and then was reacted with the DMA.

A Hull cell test performed in the way described before (3A/5 min.) showed a grain refining effect of the additive nearly up to 4.5 A/dm<sup>2</sup> according to the Hull cell scale (~ 4.5 cm from the left edge of the panel).

The question that remains here is if this grain refining effect might be due to polycondensation of dimethylamin with Epi only. This would lead to a molecule that has a proven effect in Zn electrodeposition

To further check on the principle ability of guanidin to take part in reactions with Epi in aqueous media the reaction of guanidin hydrochloride with imidazole and Epi was performed to yield a product that is comparable to the intermediate SP1092 that is currently used by COVENTYA.

In an apparatus as described before 35 g (0.51 mol) imidazol and 20 g (0.21 mol) guanidin hydrochloride are dissolved in 200 ml of H<sub>2</sub>O. The mixture is heated to 45 °C. Afterwards 80 g / 67 mL (0.92 mol) Epi are added slowly and the temperature is kept below 55 °C for most of the time during addition. The mixture is then heated to reflux at 99 °C for 2h (→ TKT 1-20).

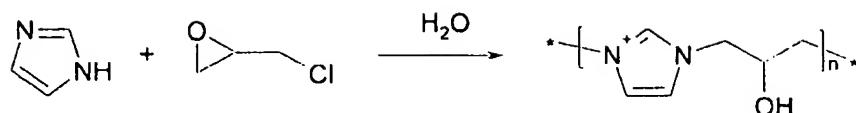


The resulting yellow solution is subjected to a Hull cell test as described before (3 A / 5 min.). The panel obtained is semi bright up to 5 cm from the left edge with some structure/pitting and bright for the remaining 5 cm with some stripes in the lcd. It also shows some pitting over the whole cd-range.

The IR spectrum after evaporation of excess water shows bands for the amino functionality and the guanidino group as well as for CH<sub>2</sub>-groups and C-OH functionality. From the spectra it can not unequivocally be concluded if the guanidin is part of the polymer backbone or not.

To further elucidate the role of the guanidin a reaction product of imidazol with Epi (see e.g.: Intermediate 82185) was produced as comparative example. The general appearance of the product, the IR spectrum and the performance in Hull cell test were compared.

40 g (0.59 mol) imidazol are dissolved in 200 mL H<sub>2</sub>O. The yellow solution is heated to 60 °C and 51 mL / 60 g (0.65 mol) Epi are added over 20 min. while the temperature is allowed to rise to 96 °C. The mixture is then heated to reflux for 3h. The resulting yellow solution has a pH of 5.9 and is free of any precipitate (→ TKT 1-27).



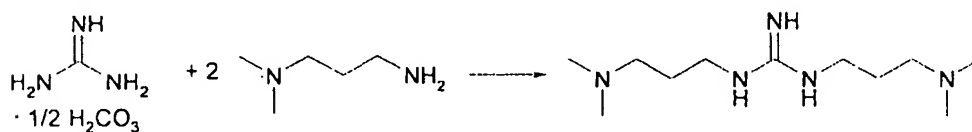
The Hull cell test (3 A / 5 min.) shows a panel that is nearly identical to the one described above for the guanidin/imidazol/Epi product. From left to right (hcd to lcd) the panel is semi bright to matte on the first 4 cm with a bright area on the following 6 cm and some stropes in the lcd. The hcd half also shows some structure/pitting.

The IR spectrum is virtually identical to the one of the GC/IMZ/Epi product except for the lack of a band for the C=N double bond.

The results obtained strongly indicate that the guanidin is not or only to a minor degree taking part in the reaction with Epi when these are performed in aqueous media! The excess Epi is in these cases probably hydrolysed to a large degree.

In order to establish a different route to a product with the desired properties as a brightening agent a different starting material was chosen. According to Bill Eckles nucleophilic substitution on guanidin by dimethylaminopropylamin (DMAPA) is possible by reacting guanidin carbonate with DMAPA without solvent.

In a first trial 22.5 g (0.12 mol) of guanidin carbonate (GC) and 63 mL (0.48 mol) of DMAPA were heated to reflux in a one necked flask with condenser and magnetic stirring.



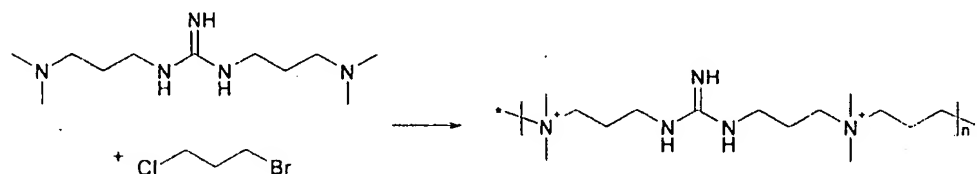
After refluxing for 5 h the amount of solid had been reduced and the liquid phase had attained a yellow colour. After 13 h at reflux the product was obtained as a very viscous amber oil ( $\rightarrow$  TKT 1-13). The IR spectrum allowed the product to be identified as identical to the substance that had been synthesised before.

The amber oil was found to crystallise in large part after standing at room temperature for 1 week. This indicates that the material contains impurities like unreacted starting material or decomposition products (the amber colour also indicates that).



In order to form a polymer with the desired properties this unit has to be linked by a suitable spacer. To introduce a trimethylen bridge between the quaternised N-centres the material can be reacted with trimethylenchlorobromide (TMCB).

50 g (0.22 mol) of the Bis-dimethylaminopropyl-guanidin and 34 g/ 21.5 mL (0.22 mol) of TMCB are mixed in a three necked flask with condenser, internal thermometer and magnetic stirring. The ingredients are thoroughly mixed and then the mixture is heated to reflux. After a few minutes of heating the mixture suddenly forms a very voluminous foam. The mixture is then heated to reflux for 1 h (take care of stirring; the mixture is very viscous). After cooling to room temperature an amber solid is obtained. The residue is dissolved in 126 mL of water to form a 40% (w/w) solution of the desired polymer ( $\rightarrow$  TKT 1-17).



The IR spectrum of the material obtained shows bands for the guanidine functionality as well as significant contributions of CH-groups. In a first Hull cell test as described before (3A / 5 min.) the material showed very promising results. The panel was grainrefined *and bright* up to 1 – 2 mm from the hcd edge. Even after 15 minutes at 3 A this aspect is retained (see picture below).



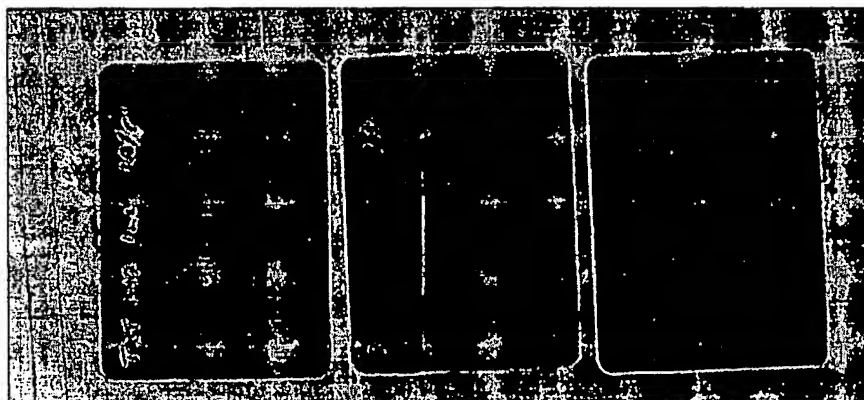
To further examine the properties of the product as a brightening agent comparative Hull cell tests were performed. Hull cell panels were plated for 5 min. at 3 A in a plating bath containing approx. 11.5 g/L Zn, 4 mL/L ANC WC, 0.8 mL/L ANC Purifier and respectively: a) 4 mL/L of TKT 1-17 (40%), b) 2.8 mL/L BC 636 (62 %) or c) 3.2 mL/L BC 915 (52 %) (The different concentrations in mL/L provide for equal

concentrations in g/L). BC 636 is a Mirapol WT clone by Brook-Chemicals-Inc. while BC 915 (also by Brook-Chemicals-Inc.) is a reaction product of urea, DMAPA and TMCB.

The panels were compared concerning their aspect and also concerning metal distribution and efficiency. X-ray measurements were taken at 2.5 (d1) and 7.5 cm (d2) from the left panel edge.

While the aspect of the panel plated using the new molecule is much better than with the comparative examples, the metal distribution is better with the Brook Chem. materials. It might be interesting to see if this might be due to e.g. a difference in the degree of polymerisation of the materials and if this could be improved for the new molecule.

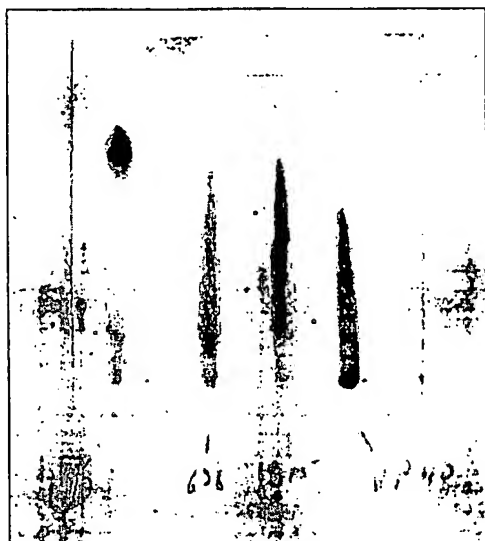
	aspect	d1/ $\mu\text{m}$	d2 / $\mu\text{m}$	d1/d2
a)	1 mm rough/grey in hcd, rest bright (with pitting)	4.7	2.0	2.35
b)	semi-bright - matt over complete cd-range	2.6	1.8	1.44
c)	semi-bright - matt over complete cd-range	2.5	2.0	1.25



Unfortunately qualitative comparison of molecular weights between the intermediate and the Brook Chem. material by HPLC proved impossible with the available equipment due to lack of UV-absorbers in the compounds. Thin layer chromatography however gives strong indication that the molecular weight of the material produced is decisively lower than that of the Brook Chem. products.

The picture below shows a TLC of from left to right, the product, BC 636, BC 915 and RP 110 (reaction product of piperazin, Epi and DMA). The TLC was performed on

Cellulose with Aceton/H<sub>2</sub>O (2:1) as eluent. The reaction product obtained here obviously has a much smaller  $R_f$  value than the Brook Chem. materials, which corresponds to a higher mobility which in turn indicates a lower degree of polymerisation. The RP 110 seems to have the highest degree of polymerisation (The poor quality of the chromatograms is due to high concentrations of the applied samples, damaging of the cellulose bed during sample application and nonuniformity of the materials).

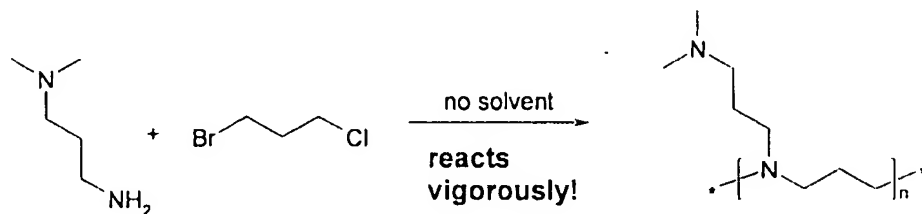


It is important to note that also other causes might be responsible for the insufficient metal distribution. As stated above the reaction of guanidin with DMAPA in the first step yielded a product that was obviously not of highest purity. Also, the reaction of this intermediate with TMCB to yield the desired polymer proceeds under conditions that are not necessarily optimal to get a high molecular weight (foam formation, etc.).

Incomplete reaction in the first step means that in the second step unreacted starting material is available to polymerise with TMCB. From the trials performed by now one can conclude that unreacted guanidin will probably not react with the TMCB. The DMAPA on the other hand is a good reaction partner for the linker. To evaluate the effect of a TMCB/DMAPA polymer the material was prepared.

In a first attempt 51 g / 63 mL (0.49 mol) Dimethylaminopropylamin and 75 g / 47 mL (0.49 mol) Trimethylenchlorobromide were mixed in a flask. Before the mixture could be heated the components reacted vigorously and the mixture erupted out of the

flask onto the ceiling of the laboratory. A small amount of the formed material could be recovered from the flask ( $\rightarrow$  TKT 1-29).

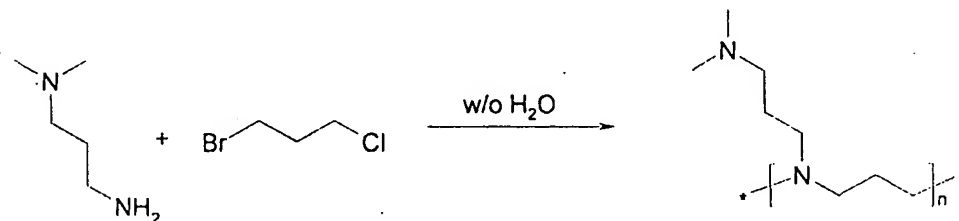


The orange to brown very hygroscopic solid easily dissolves in water. The IR-spectrum is dominated by  $\text{CH}_2$  bands and bands for ammonium ion functionalities. A Hull cell test was performed with a 30 % solution of the material as described above. The panel obtained showed ca. 3 mm of rough/grey deposit on the hcd edge. The rest was semibright/bright and very uniform without stripes or pitting. The thickness ratio between 7.5 and 2.5 cm was 1.8.

#### Outlook:

Since the product obtained in the last experiment shows some promising properties it was decided to follow this route more carefully to obtain more pure material in a practicable fashion. Parallel to that the routes mentioned before will be investigated for ways to superior brightening agents.

The reaction of trimethylene chloro bromide (TMCB) with (dimethylamino propylamine) was repeated under controlled conditions.



159 m / 129 g (1.26 mol) DMAPA was put in a reaction flask and heated to reflux (130 °C). 125 mL / 199 g (1.26 mol) TMCB was added dropwise. During the addition the reaction mixture became more viscous and obtained a yellow colour. The temperature rose up to 170 °C. After adding half the amount the added TMCB started to react very violently and the addition was stopped. The mixture was cooled to 50 °C and 150 mL of  $\text{H}_2\text{O}$  were added. The solution was again heated to reflux (107 °C)

and the remaining TMCB was added within 1h (still reacts very strongly). After the addition was completed the viscous solution was refluxed for an additional 1h. After cooling to room temperature the dark orange, viscous oil was mixed with further 240 mL H<sub>2</sub>O to obtain a 40% (w/w) solution (pH 5.5) (→ TKT 1-31). From the bottom of the flask ~ 3 mL of a clear liquid could be separated. The liquid was identified by IR to be TMCB.

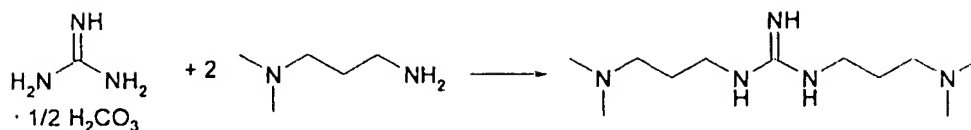
The IR spectrum of the product after evaporation of excess water showed strong bands for ammonium moieties but was otherwise uncharacteristic (which comes as no surprise considering the functional groups present in the starting materials).

The material was subjected to plating tests in the way described before (1 mL ANC WC, 0.2 mL ANC Purifier, 3 A / 5 min). Addition of 1 mL of the product solution led to a bright to semi bright Hull cell panel. The thickness ratio between the points at 2.5 cm and 7.5 cm from the left edge was 1.4. Unfortunately the product produced a massive layer of a very stable white foam. Reducing the amount of product added to 0.5 mL still produces a large amount of foam but the panel is only bright up to 6 cm from the right edge and the hcd area is very rough and grey.

Due to this experience it was decided to run the reaction once more but this time with H<sub>2</sub>O as solvent from the beginning. The same amount of amine as in the trial before was dissolved in 200 mL H<sub>2</sub>O and heated to 50 °C. Afterwards TMCB was added over 1 h while the temperature slowly rose to 100 °C at which point the solution began to reflux. The homogenous mixture was refluxed for 1 h. After cooling to RT a separate liquid phase was observed. A volume of ca. 5 mL TMCB was recovered. The mixture itself had turned into a light yellow highly viscous somehow rubber like solid. On addition of 328 g of water the material could be poured out of the flask only after strong mechanical manipulation (I nearly broke the flask) (→ TKT 1-41).

The highly polymeric residue did partly dissolve in excess water. The IR spectrum showed differences as compared to the material obtained before but was inconclusive as far as the structure is concerned. In the Hull cell test the material showed less good brightening properties (this may be due to low concentration since it was difficult to determine the amount added to the bath).

To improve the performance of the reaction product of Guanidin DMAPA and TMCB the first step of the reaction was repeated on a larger scale to improve the yield and determine the effect of the reaction conditions on completion of reaction.



135 g (0.75 mol) guanidine carbonate and 307 g/ 378 mL DMAPA were mixed in a flask with internal thermometer and condenser. The suspension was heated to reflux. During the first 11 h the temperature of the solution was ~ 127 °C. After that all solids had disappeared and the temperature began to rise to 154 °C after 17 h. At this point a white solid began to form in the upper part of the condenser. After 21 h of reflux the reaction was stopped. After cooling to room temperature a highly viscous, opaque, amber oil was obtained in the reaction flask (~335 g) (→ TKT 1-34).

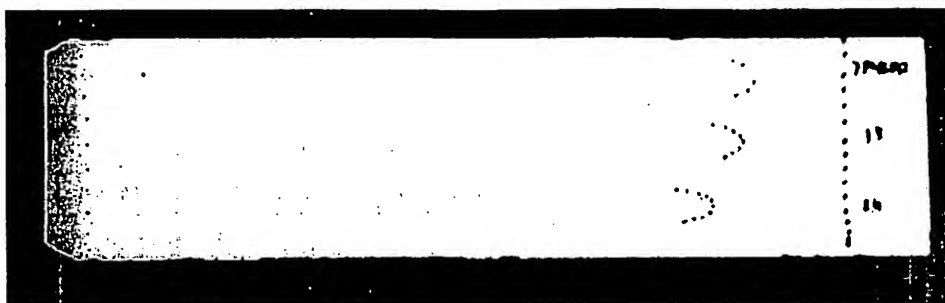
The white solid formed in the condenser could not be clearly identified although strong indication was found that it was ammonium carbonate (dissolves in acid with strong gas evolution, strong smell of  $\text{NH}_3$ ).

The IR spectrum of the amber oil was virtually identical to the one obtained in the trial before.

100 g (0.44 mol) of the material and 43 mL / 68 g (0.44 mol) TMCB were mixed in a reaction flask with condenser and internal thermometer. The mixture was stirred for 5 minutes. During that time the temperature rose at first slowly the very fast to 168 °C and a yellow foam was formed in the flask. During the reaction a white fog that smelled strongly of ammonia was driven out of the reaction vessel (→ TKT 1-41).

The residue was dissolved in 168 g of water to obtain a ~ 50 % solution. The IR spectrum of the residue was identical to the one of the material obtained before. In the Hull cell test that was performed as described above a panel was obtained that was grain refined and semi bright over the whole cd range with a thickness ratio of 2.2 (2.5 / 7.5 cm).

The high reactivity of the material indicated that there was still unreacted DMAPA present (as described before DMAPA and TMCB react violently when mixed). On the TLC shown below DMAPA (top) the material from the first trial (center) and the material from this trial (bottom) are compared. As can easily be seen the  $R_f$  values are very similar but not identical. On this basis it is therefore very difficult to say what is really causing the insufficient performance of the obtained material.



Nevertheless, the results obtained so far indicate that with the chosen starting materials and procedures a complete and fast conversion of guanidin to bis(dimethylaminopropyl)-guanidin is probably not feasible.

A way to improve the yield and specificity of this reaction may lie in the reaction conditions and starting materials.

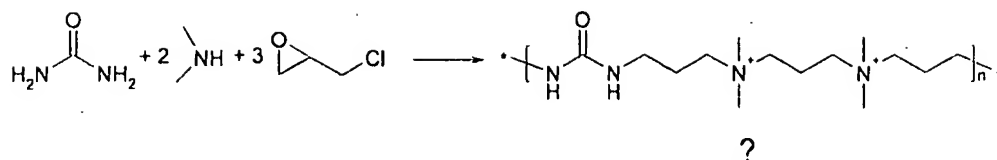
A different route to obtain a product that contains the required functional groups may be the reaction of urea and dimethylamin with different linkers. As compared to guanidin salts urea should be more easily attacked electrophilically.

In a first test urea was reacted with Epi to estimate the principal feasibility of such a route.



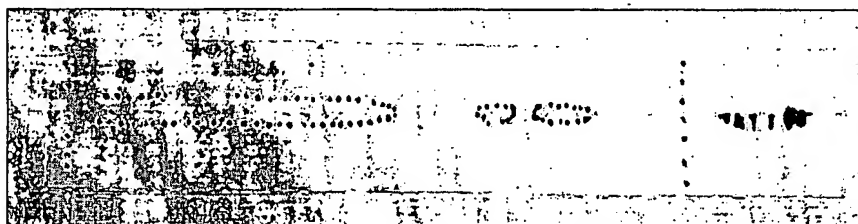
In a flask equipped with thermometer dropping funnel and condenser 15 g of urea (0.25 mol) was dissolved in 60 mL of H<sub>2</sub>O and heated to reflux. 19.5 mL / 23 g of Epi (0.25 mol) was added over 15 min. and the mixture was refluxed for 1 h. After that a clear nearly colourless solution was obtained. After evaporation of excess water the IR-spectrum of the product showed a shift of the C=O-band of the urea moiety and additional bands for CH<sub>2</sub> groups and OH functionalities. Obviously a reaction had taken place. The product was not characterised any further (→ TKT 1-43).

After establishing the principal possibility of reacting urea with epi it was decided to include dimethylamine in the reaction to generate quaternary ammonium moieties in the polymer.



30 g urea (0.5 mol) and 112.5 g / 126.4 mL DMA (40%) were dissolved in 150 mL H<sub>2</sub>O and heated to 85 °C. 120 mL / 142 g epi (1.53 mol) were added over 40 min. After stirring for 10 min. at 90 °C the mixture was heated to reflux for 2h while the temperature of the solution slowly rose from 94 °C to 101 °C to obtain a slightly yellow, oily liquid (pH 6.4) (→ TKT 1-45).

The IR spectrum of the mixture showed that urea had reacted. Besides that bands were found that matched in part the IR spectrum of the product of DMA and epi. The TLC shows that the mixture is not completely homogeneous and contains low molecular weight components (cellulose, acetone/H<sub>2</sub>O 3:1)

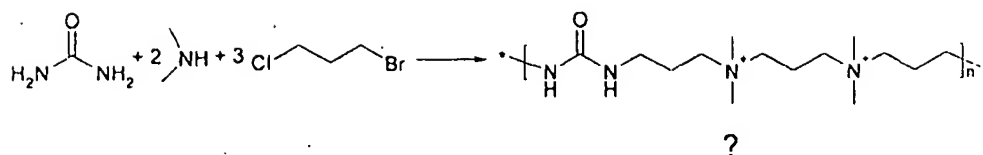


The Hull cell test (3A / 5 min) yields a panel that is grey and dull on the first 3 cm and semi bright over the rest. The metal distribution between 2.5 and 7.5 cm is 2.1. The extended spot at the bottom of the chromatogram indicates that there is indeed some polymeric material present. It is however not as efficient a brightener as required.

Further experiments on this type of material are currently in progress.

In order to further evaluate different ways to facilitate formation of brightener compounds starting from carbonic acid amide derivatives the reaction of urea, dimethylamin (DMA) and trimethylene chlorobromide (TMCB) was performed in aqueous solution.





15 g urea (0.25 mol) and 63.2 mL / 56.3 g DMA (40 %) ( 0.5 mol) were dissolved in 200 mL H<sub>2</sub>O and heated to 50 °C. 78 mL (0.79 mol) TMCB was added slowly while the temperature was increased to 90 °C. After addition was complete the mixture was heated to reflux for 5h (→ TKT 1-49). After this time a separate phase of TMCB was still present at the bottom of the flask.

To test the reactivity of the material 10 mL Dimethylamino propylamin (DMAPA) were added. The immediate temperature rise showed that the expected exothermal reaction took place. After 1h reflux unreacted TMCB was still found.

The TMCB phase was separated (35 mL) and identified by IR. The Hull cell test with the upper phase showed grain refining effect only in the low cd region of the panel.

Obviously the low solubility of TMCB in aqueous media again lead to incomplete reaction.

Since the reaction with epichlorohydrin described above seemed to have gone completely it was decided to repeat this with a different reaction sequence.

30 g urea (0.5 mol) were dissolved in 100 mL H<sub>2</sub>O and heated to 75 °C in a three necked flask with internal thermometer, condenser and dropping funnel. 80 mL Epi (1.0 mol) were added over 25 min. while the temperature was allowed to rise to 90 °C. The dropping funnel was rinsed with 25 mL H<sub>2</sub>O and the mixture was stirred for 45 min at 90 °C. After that 127 mL DMA (40%) (1.0 mol) were added in 20 min while the temperature was kept between 85 °C and 95 °C. The funnel was again rinsed with 25 mL H<sub>2</sub>O. Finally 40 mL Epi (0.5 mol) were added within 7 min. while the mixture was allowed to reflux. After refluxing for an additional 2 h the temperature had reached 102 °C and the heat was turned off. After cooling to RT a very slightly yellow solution was obtained (→ TKT 1-65).

The Hull cell test (3 A / 5 min. ) with 1 mL of the solution yielded a panel that was grey and slightly dendritic up to 4 cm and semi bright over the rest of the panel.

These results indicate that a reaction product that has similar or superior properties than Mirapol WT is not easily obtained by this synthetic route. Therefore it was

concluded to concentrate further on the improvement of guanidin derivatives described in the last report.

In order to improve the reaction of guanidin with dimethylamino propylamin a different experimental setup was chosen as compared to the experiments reported before.

113.8 g guanidin hydrochloride (GHC / 1.19 mol) and 300 mL / 243.6 g dimethylamino propylamin (DMPA / 2.38 mol) were mixed in a 1L three necked flask equipped with condenser, internal thermometer, electric shaft stirrer and electric heating mantle. The guanidin hydrochloride dissolved immediately. The mixture was heated to reflux for 8h. During this time the temperature rose to 210 °C and the colour changed from colourless to amber. After cooling to room temperature a highly viscous amber substance was obtained (→ TKT 1-47). The IR spectrum showed the expected bands for the C=N bond and the different methyl and methylene groups together with the NH-bands. The results indicate that this experimental setup is a big improvement. It reduces the reaction time and seemingly also the yield and purity of the product.

The product obtained in this way was reacted with trimethylene chlorobromide (TMCB) in different ways to evaluate the possible use as a brightening agent.

In a first reaction 43 g guanidin•DMPA (0.19 mol) was mixed with 18.6 mL TMCB (0.19 mol) in a flask with magnetic stirrer and condenser. The mixture was carefully heated. After approx. 10 min. the mixture erupted and formed a yellow foam in the flask. This solid residue was dissolved in 75 mL H<sub>2</sub>O to give a ~ 50% solution (→ TKT 1-51). A very small amount of unreacted TMCB could be recovered by phase separation. The IR spectrum of the dry product showed that the bands for the aminomethyl groups had shifted in the expected way and the band for the methylene groups had increased in intensity and also shifted.

In the plating test (3 A / 5 min.) the material produced a bright panel with thickness ratio of 1.7 between 2.5 and 7.5 cm from the left edge.

Since this way of producing the polymer is not by any means an option for industrial scale and since the metal distribution obtained with this material is not satisfactory a different experimental setup was tested.

229 g guanidin•DMPA (1mol) were put into a three necked flask with internal thermometer, shaft stirrer, dropping funnel and heating mantle and heated to ~90°C.

157 g / 98 mL TMCB (1 mol) were added slowly over 35 min. During this time the temperature rose to  $\sim 170\text{ }^{\circ}\text{C}$  and the mixture became extremely viscous. After an additional 30 min the residue could no longer be stirred. After cooling to room temperature 386 mL of water were added to obtain an approx. 50% solution ( $\rightarrow$  TKT 1-53).

The IR spectrum was basically identical to that of the material obtained before. In the Hull cell test (3A / 5 min) a bright panel was obtained the thickness ratio of the deposit at 2.5 and 7.5 cm from the left edge was determined to be  $r = 1.8$ . A comparative panel obtained with BC 915 (urea•DMPA + TMCB) was found to be only semi bright but with a thickness ratio of  $r = 1.2$ .

The second step in the production of Mirapol WT is performed in aqueous solution. Therefore this should also be an option for the reaction of guanidin•DMPA with TMCB.

150 g of guanidin•DMPA (0.66 mol) were dissolved in 170 mL  $\text{H}_2\text{O}$  and heated to  $80\text{ }^{\circ}\text{C}$ . 65 mL / 103 g of TMCB (0.66 mol) were added over 30 min. During this time the temperature was allowed to rise to  $100\text{ }^{\circ}\text{C}$  where the mixture started to reflux. The mixture was refluxed for 4 h while the temperature slowly rose to  $105\text{ }^{\circ}\text{C}$ . After cooling to room temperature approx. 2 mL of unreacted TMCB were separated ( $\rightarrow$  TKT 1-56).

The IR spectrum of the yellow product was identical to the one obtained from the reactions without solvent. The hull cell test yielded a semi bright panel. The degree of brightness of the other materials was not quite reached. The thickness ratio between the points at 2.5 and 7.5 cm from the left edge was determined to be  $r = 1.7$ .

To determine whether the pure metal distribution and the fact that unreacted TMCB was found in virtually every reaction is connected the reaction might be performed in a less polar solvent. Glycerol is a good candidate because it is polar enough to dissolve the polymer, the boiling point is high enough to allow decent reaction rates and it has also been used as an additive in alkaline zinc plating. The latter would alleviate the obligation to remove the solvent.

150 g guanidin•DMPA (0.66 mol) were dissolved in 130 mL of glycerol and the viscous mixture was heated to  $90\text{ }^{\circ}\text{C}$ . 65 mL TMCB (0.66) were slowly added over 2h. The temperature rose rapidly to  $160\text{ }^{\circ}\text{C}$  and the mixture turned dark. After cooling

to room temperature an extremely viscous brown substance was obtained and a small amount (8 mL) of a colourless liquid separated on top. The colourless liquid was identified as TMCB by IR. The brown residue dissolved only very slowly in water ( $\rightarrow$  TKT 1-57). A small amount of the material was added to a hull cell. The plating test at 3A / 5 min yielded a bright panel. The thickness ratio was determined at  $r = 1.5$ .

Obviously this method to produce the desired material gave no improvement and created new problems for manufacturing on a larger scale.

An additional option to create a polymer with the desired guanidino and dimethyl-ammonium functionalities is linking the guanidin•DMPA with epichlorohydrin.

57 g guanidin•DMPA (0.25 mol) were dissolved in 80 mL  $H_2O$  and heated to 70 °C. 25 g / 21 mL Epi (0.27 mol) were added within 7 min. while the temperature was allowed to rise to 101 °C and the solution began to reflux. The solution was heated to reflux for 2 ¼ h more. After cooling to room temperature an amber solution was obtained ( $\rightarrow$  TKT 1-59).

The IR spectrum after evaporation of water corresponded to the materials obtained from reaction with TMCB but additionally showed bands for C-OH groups. The Hull cell plating test (3 A / 5 min) yielded a bright panel over the whole cd-range. The thickness ratio was determined to be  $r = 1.7$ .

None of the reaction products described above did so far show the properties that would make a superior brightener. There are two possible reasons for this behaviour. Either the guanidin group does not give the same good metal distribution as the urea, or the synthetic methods used so far do not yield polymers that have the necessary molecular weight or composition. To distinguish these possibilities it was decided to synthesise the urea derivative by the same methods and compare it with the guanidin species obtained so far.

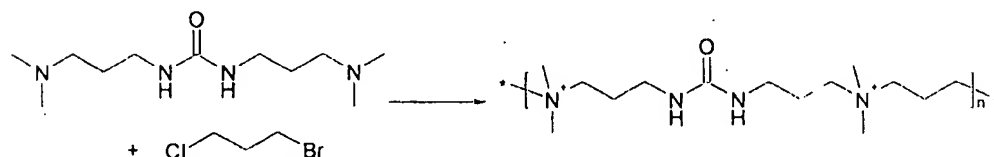


90 g urea (1.5 mol) were mixed with 378 mL DMPA (3 mol) in a three necked flask with internal thermometer, condenser, shaft stirrer and heating mantle. After heating for approx. 40 min. the mixture had reached a temperature of 125 °C and reflux, the

urea had dissolved and a gas evolution was observed. After refluxing for 3 h the temperature of the mixture had reached 260 °C, a colourless vapour was observed in the reaction flask and a colourless had formed in the lower part of the condenser. The heat was turned off and the mixture allowed to cool to RT (→ TKT 1-61).

The product was obtained as a yellow liquid. The IR spectrum corresponded to the available literature data.

In the next step the obtained urea•DMAPA was reacted with TMCB to obtain the desired polymer.

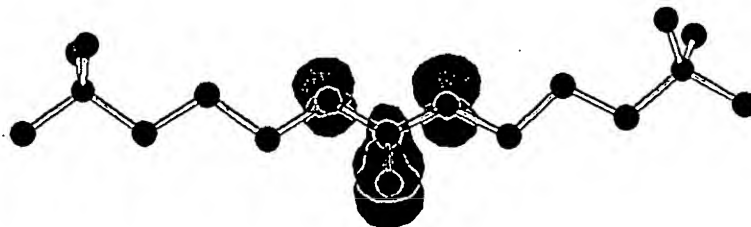


57.5 g urea•DMAPA (0.25 mol) and 39 g /25 mL TMCB (0.25 mol) were mixed and slowly heated under stirring. After ca. 10 min the mixture suddenly erupts to form a yellow solid foam (a little like polyurethane-foam). After cooling to room temperature the residue is dissolved in 100 mL H<sub>2</sub>O to yield a ~50 % solution (→ TKT 1-63). The IR spectrum of the product was found to be nearly identical to the commercially available material from Brook Chem BC 915. In the plating test (3 A / 5 min.) 1 mL of the solution was added to a Hull cell and a semi bright panel was obtained. The thickness ration a the points at 2.5 and 7.5 cm from the left edge was determined to be  $r = 1.2$ .

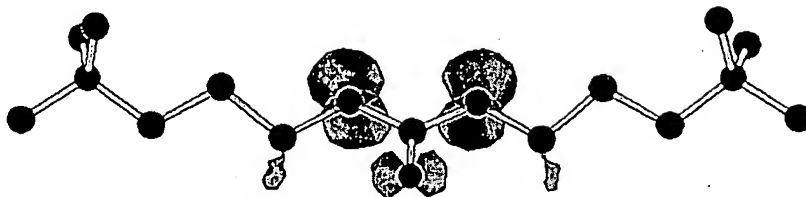
From these last results it has to be concluded that the applied synthetic methods are suitable to generate polymers that give the desired properties. Therefore the only conclusion left is that the urea moiety has unique properties to induce a good metal distribution in alkaline zinc plating bath that the guanidin function lacks. The only advantageous property of the guanidin based polymers observed is the better brightness that was found in several of the aforementioned experiments.

## HOMO

Guanadmapa – dikation:



Ureadmapa – dikation



carbon = black, oxygen = red, nitrogen = blue; hydrogen omitted for clarity

(models calculated at MP3 level, MO = canonical orbitals, 35 % P)

The illustrations above might help to explain the different activity of urea and guanidin derivatives. The pictures show the front orbitals of two model compounds for the guanidin and the urea polymer as obtained from semiempirical quantum mechanical calculation (PM3 – method). As can be seen in the guanidin derivative the homo has some contribution from the C=N double bond. In the urea case the homo is mainly made up of none-bonding orbitals at oxygen and nitrogen. This important difference in the electronic structure may well account for the different effect as a brightener in alkaline zinc baths.

The results obtained so far allow to draw the following conclusions:

It is comparatively easy to combine various simple amines and epichlorohydrin or trimethylene chlorobromide in ways to obtain polymers that give a grain refining and brightening effect. It is much more difficult to find such a polymer that has not been described in the literature sometime before. And judging from the obtainable literature sources and the knowledge present at Coventya and Taskem it seems very unlikely that by following this route a polymer can be obtained that additionally shows the

positive effect on metal distribution that modern alkaline zinc and zinc alloy plating baths recommend.

All results indicate that the superior properties of Mirapol WT depend to a large extent on the presence of the urea group. This in itself is not a surprising insight. It is surprising though that substitution of the oxygen by other groups as for example an NH (as in guanidin) dramatically alters the performance of the polymer as a zinc brightener even if the basic structure is maintained.

While the use of Mirapol WT as an additive in zinc or zinc alloy plating baths can be considered as common state of the art, the use of derivatives is partly covered by patents. US5405523 (Eckles) covers the use of ureaDmapa and GuanaDmapa derivatives linked with different difunctional alkylidene or hydroxyalkylidene (i.e. Epi) spacers. WO0050669 (Macdermid) covers the use of propylene dihalides as spacer precursors. To find a molecule that has equal or superior properties as compared to WT one has to circumvent the restrictions imposed by these patents.

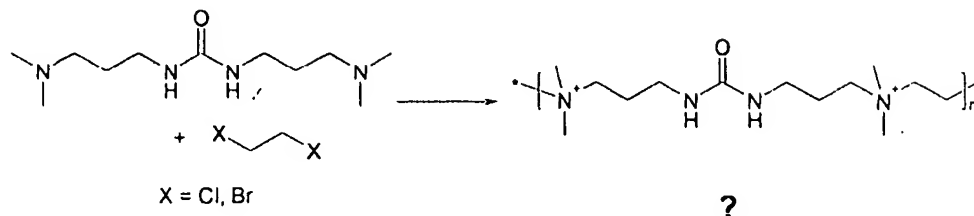
Taking into account the results obtained so far the following options for further experiments are the most promising:

- 1) Linking ureaDMAPA with different spacer units: ethylene, epi
- 2) Copolymerising ureaDMAPA and guanaDMAPA
- 3) Linking ureaDMAPA with different spacer units in the same polymer: e.g. TMCB + Epi
- 4) Copolymerising ureaDMAPA with other amines

1) would circumvent the existing patents in case of ethylene. In case of using epi only the Eckles patent would apply. Both molecules have not yet been tested to our knowledge. 2) might combine the superior metal distribution of the urea derivative with the better brightness observed in some cases with the guanidin based molecules. 3) would in any case circumvent all existing patents. It should be easy to do and might provide different properties(?). 4) is a strategy similar to 2). Here also the idea is to combine the good metal distribution obtained with WT with the excellent brightness obtained with other polymers.

Based on this a number of experiments was performed:

Ureadmapa was reacted with 1,2-dichloro ethane (DCE) in a first test.



57.5 g ureadmapa (0.25 mol) were dissolved in 80 mL H<sub>2</sub>O and heated to 50 °C. 25 g / 20 mL DCE (0.25 mol) were added in 15 min. while the temperature was allowed to rise to 70 °C. The now turbid emulsion was refluxed for 5 ½ h at 105. After cooling to room temperature a dark amber, offensively smelling oil was obtained (→ TKT 1-66).

The IR spectrum of the material after evaporation of water shows bands for unreacted dimethylamino groups. The Hull cell test (3 A / 5 min) yields a panel that shows a burn on the first 2 mm and is bright over the rest of the panel. After acid dipping and drying the panel is very white at first but turns brownish after several minutes. The thickness ratio of the deposit at 2.5 and 7.5 cm is  $r = 2.6!$

Since the results indicate that even after this extended reaction time the reaction is incomplete (in spite of starting decomposition → colour) the experiment was repeated with 1,2-dibromo ethane (DBE) which might give better yields due to the better leaving group character of bromide.

57.5 g ureadmapa (0.25 mol) were dissolved in 100 mL H<sub>2</sub>O and heated to 85 °C. 47 g / 21.5 mL DBE were added within 10 min. and the mixture was stirred for 2 ½ h at 70 – 90 °C. After cooling to room temperature a dark amber liquid was obtained (→ TKT 1-70).

The result of the Hull cell test was similar to the result obtained from the DCE reaction except that the burned area was more pronounced (1cm). Even the discoloration a few minutes after plating was observed.

The IR spectrum again shows signals for unreacted dimethylamino groups. Since the reaction with DBE did not give a quantitative yield of the product it was decided to react the starting materials without solvent to force a completion of the reaction.

23 g ureadmapa (0.1 mol) and 19 g / 8.6 mL DBE (0.1 mol) were mixed and slowly heated. After some minutes the mixture boiled up and turned brown. After cooling to

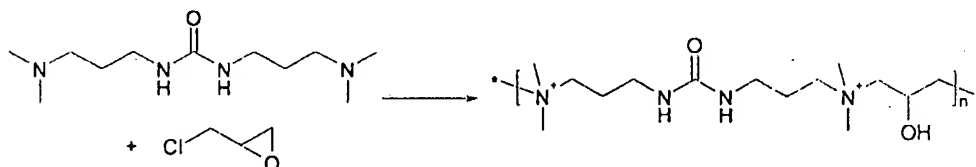


room temperature a brown glass like solid was obtained that could be dissolved in 42 mL of water to give a ~50% solution ( $\rightarrow$  TKT 1-72).

The solution in the Hull cell test turns turbid after adding 1 mL of the material. The panel obtained is burned on the first 6 mm and bright with pittings up to 9.5 cm. On the 5 mm in the lcd area the plate is partially skipped. The IR spectrum shows no signs of unreacted dimethylamino groups.

From these results it can be generally concluded that the reactions with ethyl spacers do not yield products with the needed properties. Additionally the reactions do not proceed quantitatively and yield comparatively large amounts of decomposition products. This might be due to the fact that on completed reaction two cationic nitrogen centers would be separated only by the short ethylene spacer. The electrostatic repulsion might hamper the product formation.

Linking the ureadmapa units with epichlorohydrin has been suggested in patent literature but there seems to be no application of this molecule. This is surprising in so far as epi amine reaction products are commonly used in electroplating baths.



57.5 g ureadmapa (0.25 mol) were dissolved in 80 mL  $\text{H}_2\text{O}$  and heated to 80 °C. 25 g / 21 mL epi were added within 10 min. and the temperature was allowed to rise to 104 °C. The solution was refluxed at that temperature for 1h. After cooling to room temperature a dark brown oil was obtained ( $\rightarrow$  TKT 1-68).

The IR spectrum of the material after evaporation of excess water showed bands for a small amount of unreacted dimethyl amino groups. The Hull cell test (3 A / 5 min.) yielded a panel that was semi bright over the whole cd-range with a 4 mm frosty / white area at the high cd edge. It was surprising to find, that the efficiency of the bath had been nearly completely suppressed by the additive. The thickness of the deposit was found to be less than 1  $\mu\text{m}$  at 2.5 and 7.5 cm from the high cd edge (100 % efficiency  $\sim$  12  $\mu\text{m}$  at 2.5 cm mark)!

To verify this surprising result it was decided to repeat the reaction under more controlled temperature conditions.

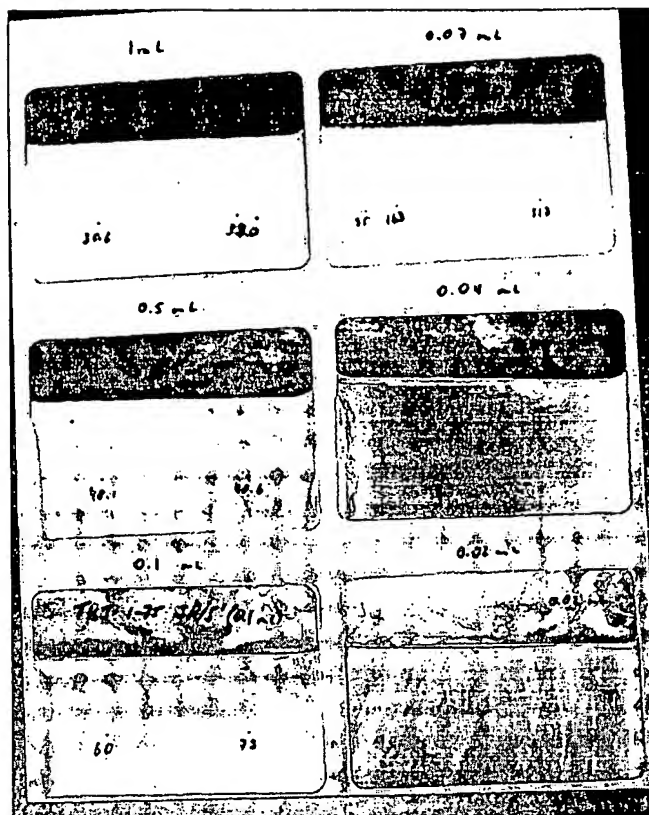
116.5 g ureadmapa (0.507 mol) were dissolved in 170 g H<sub>2</sub>O and heated to 65 °C. 51.6 g / 43.5 mL Epi (0.557 mol) were added within 20 min. and the temperature was allowed to rise to 92 °C. Afterwards the mixture was stirred 65 – 75 °C for 2h. after cooling to room temperature an amber coloured oil was obtained (→ TKT 1-75). Seemingly less decomposition products are formed under the lower temperature conditions.

The IR spectrum shows that basically all dimethylamino groups had reacted inspite of the lower temperature. The C-O stretch can be seen at 1104 cm<sup>-1</sup>.

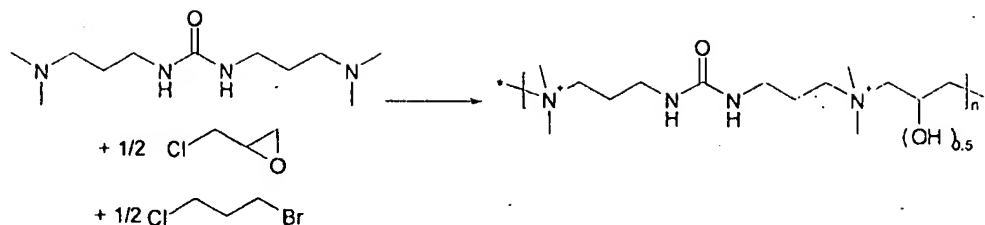
A dilution series for Hull cell testing was made to estimate the effect of the brightener at different concentrations (see picture below and table / the amounts of brightener are given in mL of concentrated product solution per Hull cell).

Obviously the product provides for extreme cathode polarisation especially in the high current density area. At lower concentrations a pattern develops that seems to indicate two different modes of activity. One polarising the high cd area and the other providing grain refinement from the low cd. No proof could be found that the mixture consists of two different products.

Brightener / mL	Aspect and thickness at 2.5 / 7.5 cm	Thickness ratio
1	1.5 mm white / frosty, rem. semibright - bright; 36 / 34 µin	1.06
0.5	dto.; 40.6 / 40.1 µin	1.01
0.1	3 mm white / frosty; rem. bright with stripes; 60 / 79 µin	0.76
0.07	1 mm white / frosty, - 2 cm bright (pitting), - 7 cm slightly grey/dull, rem. bright / striped; 163/117 µin (95 at 1.5 cm)	1.4
0.04	2 mm bright, - 9 cm grey / dendritic, rem. semibright / striped; - / - µin	-
0.02	grey / dendritic; - / - µin	-



These results initially gave the impetus for the idea of polymerising ureadmapa units with different linkers in one polymer. The general aspect obtained with the epi based polymer was an improvement in brightness as compared with the TMCB based polymers. On the other hand the inhibiting effect was far too pronounced to be of practical use. It was therefore decided to polymerise ureadmapa with TMCB and epi in one polymer.



92 g ureadmapa (0.4 mol) were dissolved in 150 mL H<sub>2</sub>O and the light yellow solution was heated to 70 °C. 31.5 g / 20 mL TMCB (0.2 mol) were added within 5 min. while the temperature was allowed to rise to 100 °C. The solution was stirred at this temperature for 25 min and then cooled down to 65 °C within 30 min. 20.2 g / 17 mL epi were added within 10 min. and the temperature was allowed to rise to 85 °C. The solution was then stirred for 2 ½ h at 70 – 80 °C. After cooling to room temperature a viscous yellow liquid was obtained (→ TKT 1-78 / TKT 1-88).

The IR spectrum of the material after evaporation of excess water is very similar to the product of the reaction with TMCB only. Additionally some bands can be seen between 950 and 1150 cm<sup>-1</sup> that can be attributed to the additional C-OH functionality. The Hull cell test yields a panel that is uniformly semibright over the whole current density range. The thickness ratio between 2.5 and 7.5 cm on the panel is  $r = 1.1$  with a very decent efficiency.

This result is very encouraging since it yields a material that gives a good metal distribution together with a moderate degree of brightness. Generally speaking the brightness obtained with this molecule can be considered a slight improvement as compared to Mirapol WT.

The extreme effect observed with the epi-only derivative is not observed and it might be interesting to see if there is an influence of the reaction sequence on the performance of the material.

60.6 g ureadmapa (0.263 mol) were dissolved in 100 mL H<sub>2</sub>O and heated to 64 °C. 13.4 g / 11.3 mL epi (0.145 mol) were added within 7 min. and the temperature was

allowed to rise to 86 °C during this time. Afterwards the solution was stirred at 60 – 90 °C for 55 min. and the solution turns more yellow. 20.7 g / 13 mL TMCB are added within 7 min. and the mixture is refluxed at 100 °C for 1 ½ h. After cooling to room temperature a dark amber, viscous liquid is obtained (→ TKT 1-82).

The IR spectrum of the material after evaporation of excess water shows that nearly all dimethyl amino groups have reacted. The pattern in the range from 950 – 1150  $\text{cm}^{-1}$  is slightly different from the one obtained with the other reaction sequence.

The Hull cell test yielded a panel that was semi bright over the whole current density range. The thickness ratio was determined to be  $r = 1.2$

Due to these observations the route chosen at first (TMCB added first and epi reacted later at lower temperatures) seems to be more promising. As already observed in the reactions with epi only, these products seem to be sensitive to high reaction temperatures. They form decomposition products that perhaps do not interfere with the plating properties. Nevertheless they lead to discoloration of the product.

With the "copolymerisation" product of ureadmapa, TMCB and epi a first molecule has been synthesised that provides for the superior metal distribution of Mirapol WT with a slightly improved brightness and – very importantly – is not covered by existing patents!

Further experiments were undertaken to improve the understanding of these reactions in general and possibly further improve the properties of the brightener.

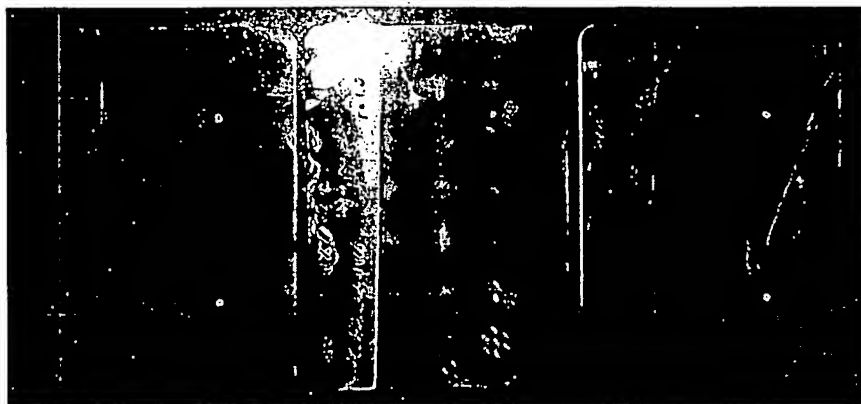
The material that showed the most promising result so far, namely the reaction product of ureadmapa, TMCB and Epi was subjected to a more thorough investigation regarding its usefulness as a brightener.

In a comparative plating test Hull cell tests were performed at 1 A / 15 min. The electrolyte was made up to contain approx. 11 g/L Zn, 125 g/L NaOH, 1 mL/HC ANC WC (EDTA sol.), 0.2 mL/HC ANC Purifier (thiourea sol.) and 2.7 mL/HC (mL / Hull Cell) RP 109 (1%) (RP 109 = 2 mol/L BPC). To these baths were added:

- 1) 2.7 mL/HC of the reaction product (10 % solution)
- 2) 2.7 mL/HC of Mirapol WT (8 % sol.)
- 3) 2.7 mL/HC BC 915 (8 % sol.)

The results can be summarised as follows (see picture below): The reaction product gives the brightest panel with some stripes in the low cd region followed by the BC 915. The Mirapol panel shows a generally more cloudy aspect. The metal distribution was determined by measuring the thickness at 2.5 and 7.5 cm from the left panel edge and calculating the ratio. The value was found to be between 1.0 and 1.2 for all panels.

The major difference was found to be in the general thickness of the deposit. Both Mirapol WT and BC 915 give deposits of approx. 150 – 180  $\mu\text{m}$  at both measurement points. The new polymer under the same conditions gives only 100 – 120  $\mu\text{m}$ ! This is a 30 – 50% lower current efficiency.



To improve this result a Hull cell test was performed with only half the amount of the polymer under the same conditions. The result was not satisfactory. A dull deposit was obtained in the medium current density range while strong cathode polarisation was still seen in high cd.

A further observation that caused some concern with this kind of material was the occurrence of latent blistering. A Jiggle cell panel was plated at 3A / 30 min (1.4 oz/g Zn, 1% of a 1% sol. of 2 mol/L BPC) with 1 % of a 10% solution of the reaction product. The plate was bright and uniform. After plating the panel was flattened out and left at room temperature. After 2 days massive blistering was observed first along the flattened bends then on the whole surface. A comparative panel that was plated with Mirapol WT under the same conditions did not show any blistering after 2 weeks.

It seems that the presence of epi linking groups in the polymer still leads to a strong polarisation of the cathode. This corresponds to the result obtained with the epi-only

polymer. Nevertheless the efficiency is better than when only using epi. Besides that this strong polarisation seems to lead to the latent blistering.

It would be interesting to see if a TMCB / epi ratio could be found, that preserves the superior brightness as compared to Mirapol WT and still gives satisfactory current efficiency. To test this ureadmapa was reacted with TMCB and epi in a 3/1 ratio.

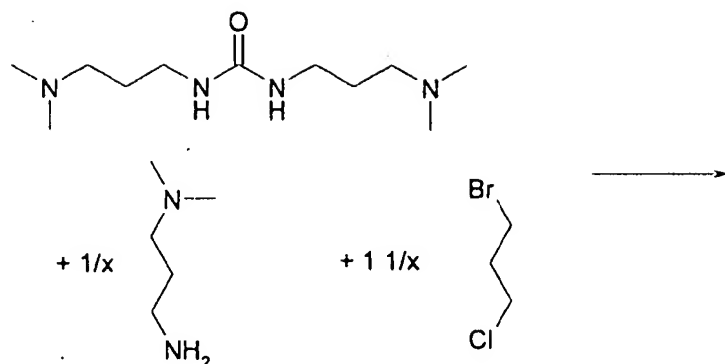
115 g ureadmapa (0.5 mol) were dissolved in 190 mL H<sub>2</sub>O and heated to 70 °C. 59 g / 37 mL TMCB (0.375 mol) were added within 20 min and the solution was refluxed for 35 min. at 100 °C. The mixture was then cooled to 60 °C in 20 min. 13 g / 11 mL epi (0.14 mol) were added in 6 min and the temperature was allowed to rise to 70 °C. The mixture was then stirred for 1 ¼ h at 60 – 70 °C. After cooling to room temperature a nearly colourless viscous solution was obtained (→ TKT 1-96).

The IR spectrum of the material shows a pattern in the region between 900 and 1200 cm<sup>-1</sup> that lies between the one observed for BC 915 and the one for the 1/1 reaction product.

The Hull cell test yielded a panel that was semibright to bright over the whole cd range. The general aspect is comparable to the 1/1 reaction product. The thickness ratio was determined as  $r = 1.3$ . At comparable concentration the efficiency was found to be nearly twice as high as the efficiency with the 1/1 product.

Seemingly the drawbacks of the use of epi can be overcome by increasing the TMCB/epi ratio in the reaction while retaining some of the advantages.

A different route that was to be investigated is the co-polymerisation of ureadmapa with other amines. It was observed before that the reaction product of TMCB and DMAPA under some conditions gave very bright panels. It was also observed that in some cases when incomplete reactions led to incomplete quaternisation of dimethyl amino groups improved brightness was observed. On the background of these results it was decided to co-polymerise ureadmapa with fractional amounts of DMAPA and TMCB.



In a first experiment 57.5 g ureadmapa (0.25 mol) and 2.5 g / 3.1 mL DMAPA (0.025 mol) were dissolved in 150 mL of H<sub>2</sub>O and the clear slightly yellow solution was heated to 80 °C. 43.2 g / 27.1 mL TMCB (0.275 mol) were added within 8 min. while the temperature was allowed to rise to 95 °C. The mixture was then heated to reflux for 2h at 100 °C. After cooling to room temperature a clear, nearly colourless, viscous solution was obtained (→ TKT 1-80).

The IR spectrum of the material after evaporation of excess water was surprising. No bands for unreacted dimethyl amino groups could be found. Generally the spectrum looked nearly identical to that of BC 915. A possible explanation for this observation might be that instead of the primary amine the tertiary amine group reacts preferentially with the TMCB.

The Hull cell test (3 A / 5 min.) yielded a semi bright panel with some stripy aspect in the lcd region. The thickness ratio was determined to be  $r = 1.3$ . Using a 10% diluted solution of the material a bright to semi-bright panel was obtained that showed no stripy aspect. This indicates that this kind of defect might be due to an over dosage of the polymer. Generally speaking the aspect found does not fulfil the expectations.

The brightness is not dramatically improved as compared to BC 915.

To further investigate this surprising result the experiment was repeated with a higher amount of DMAPA relative to ureadmapa. 115 g ureadmapa (0.5 mol) and 10.2 g / 12.6 mL DMAPA (0.1 mol) were dissolved in 220 mL H<sub>2</sub>O and heated to 85 °C. 94.5 g / 59 mL TMCB (0.6 mol) were added during in 23 min. while the temperature was allowed to rise to 98 °C. The solution was then refluxed for 2h at 101 °C. After cooling to room temperature a nearly colourless, clear, viscous solution is obtained.



The product exhibits a strong smell that might be attributed to hydrolysis products of TMCB ( $\rightarrow$  TKT 1-85).

The IR spectrum of the material after evaporation of excess water again shows no signals for unreacted dimethyl amino groups.

In the Hull cell test a panel is obtained that shows a semi bright aspect with a slight matte haze over the whole cd range. The thickness ratio is determined as  $r = 1.3$ . Using a 10 % solution of the product a semibright panel is obtained that shows some spots in the hcd - mcd area.

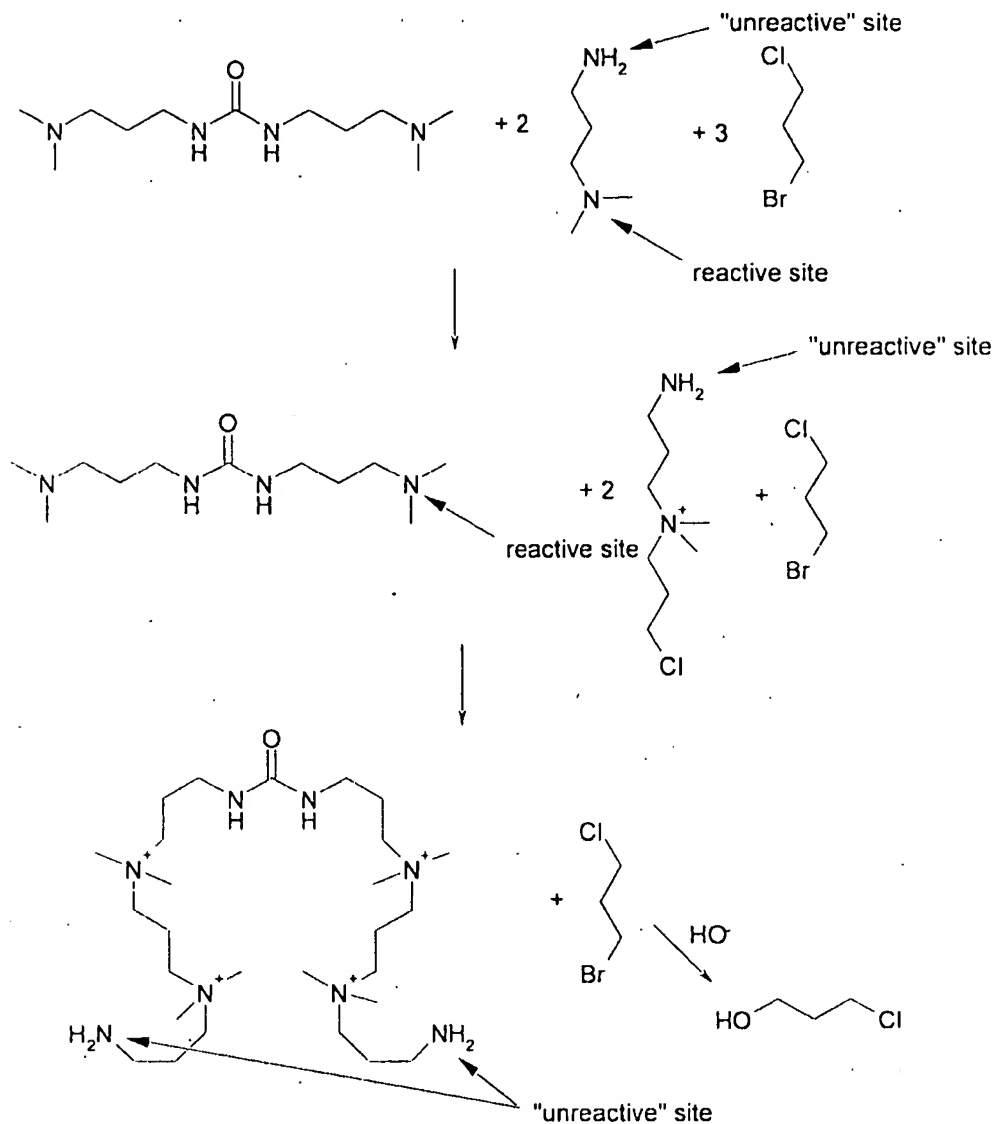
These observations lead to the following questions. Why does the product contain no free dimethyl amino groups? Why does the Hull cell test show these strange defects in aspect? Why does the product exhibit this strong smell of alcohol?

The scheme below shows a possible explanation for these observations.

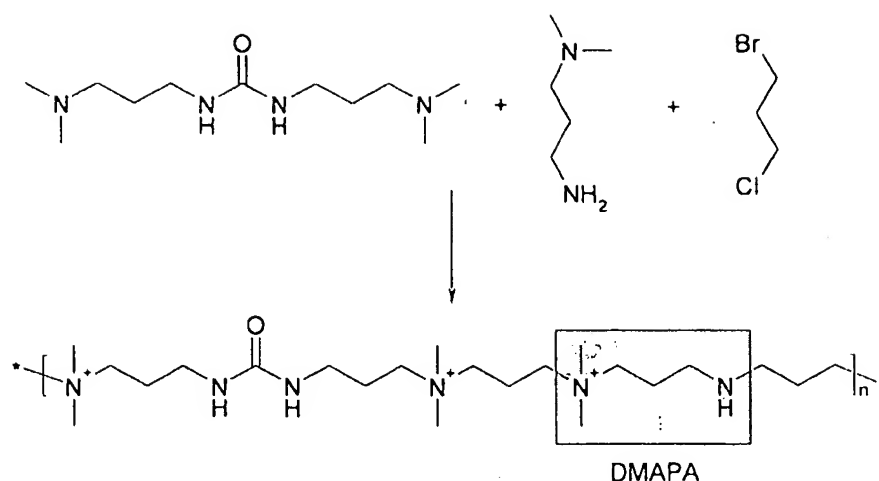
As was observed before in some reactions with TMCB the nucleophilicity of the amines does not allow a complete conversion of the material and unreacted TMCB is left even after extended reaction times. It is therefore reasonable to assume that the primary amino function in DMAPA is not able to react with TMCB. If the TMCB reacts with the tertiary amino function only then this reaction is a chain terminating step as described by the scheme above. The remaining unreacted TMCB would probably be partly hydrolysed under the basic reaction conditions.

This would explain why no unreacted dimethyl amion groups are observed. The spotty aspect of the Hull cell panels is probably caused by the alcohol that is formed during hydrolysis of TMCB. The alcohol has only limited solubility in the plating bath and precipitates in the cathode film. This precipitation could cause the kind of defect observed.

Example for chain-terminating reaction with TMCB-hydrolysis



Since the DMAPA is present at only a fraction of the ureadmapa concentration a polymer will be formed in these reactions that gives the observed properties. It is also reasonable to assume that the primary amine will in small part react with TMCB. An example for the structure of the polymer thus obtained would have the structure shown below.



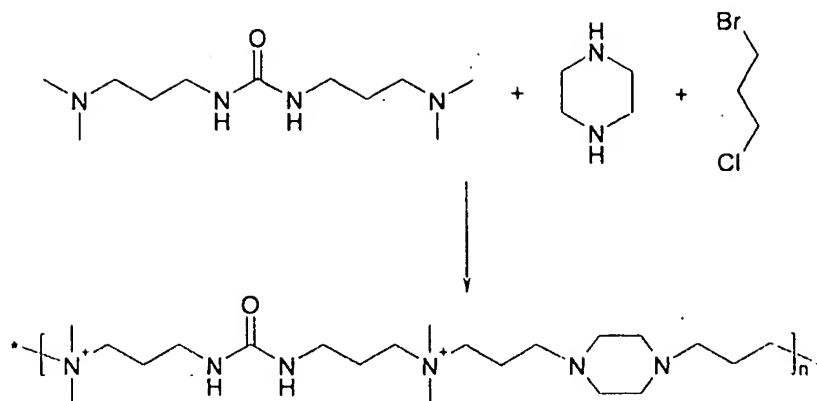
Since epichlorohydrin should be able to react with both amino functions of DMAPA it was decided to perform a comparative experiment with epi as the linking group.

115 g ureadmapa (0.5 mol) and 10.2 g / 12.5 mL DMAPA were dissolved in 190 g H<sub>2</sub>O and heated to 60 °C. 61.1 g / 51.6 mL Epi were added in 25 min. while the temperature rose to 85 °C. The mixture was then stirred for 2h at 60 – 70 °C. After cooling to room temperature a light yellow viscous liquid was obtained (→ TKT 1-89).

The IR spectrum showed that all dimethylamino groups had been quaternised. Additionally the expected bands for the C-OH function at 950 to 1100 cm<sup>-1</sup> were observed.

The Hull cell test yielded a panel that was semi bright to bright over the whole cd range. Unfortunately again a very low current efficiency was observed with a metal distribution of  $r = 0.98$ . Obviously the epi reaction product again is a far too strong polariser to be useful as a brightener.

A class of polymers that gives very bright Zn deposits are the ones based on piperazin epi reactions. It would therefore be of interest to know if piperazin can be copolymerised with ureadmapa to give bright deposits and if piperazin is nucleophilic enough to react with TMCB.



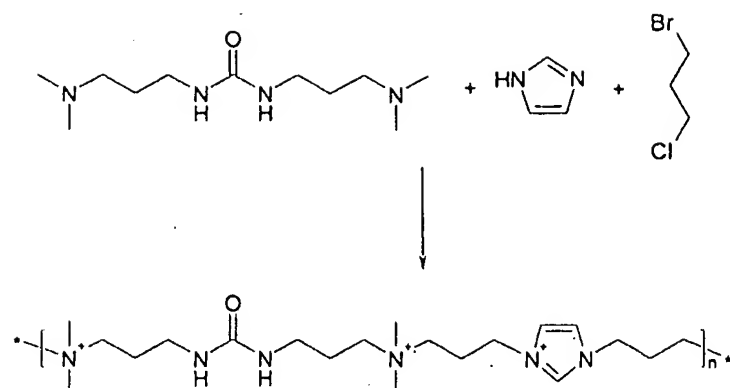
57.5 g ureadmapa (0.25 mol) and 4.3 g piperazin (0.05 mol) were dissolved in 75 mL  $\text{H}_2\text{O}$  and heated to 80 °C. 47.2 g / 29.5 mL TMCB (0.3 mol) were added in 20 min while the temperature was allowed to rise to 103 °C. The solution was refluxed at 100 – 104 °C for 2h. After cooling to room temperature a light yellow, viscous liquid with a strong smell of halogenated alcohol was obtained. (→ TKT 1-92).

The IR spectrum of the material after evaporation of excess water resembled the one of BC 915. An additional band at  $2709\text{ cm}^{-1}$  was observed that was assigned to the piperazin unit.

The Hull cell test yielded a semi bright panel with a hazy / stripy deposit in the mcd – lcd area and some spots in the hcd area. The thickness ratio was determined as  $r = 1.4$  with a mediocre efficiency.

Seemingly piperazin is also not nucleophilic enough to give a complete reaction with TMCB and hydrolysis products are formed (smell, spots, etc.). The relatively low efficiency of this formulation is somewhat surprising.

A further candidate for co polymerisation that might contribute to the overall brightness is imidazole. Imidazole epi polymers are well known brightening additives for Zn baths. Also imidazole provides at least one tertiary amine nitrogen per molecule that should be nucleophilic enough to react with TMCB.



115 g ureadmapa (0.5 mol) and 6.8 g imidazol (0.1 mol) were dissolved in 220 mL  $\text{H}_2\text{O}$  and heated to  $95^\circ\text{C}$ . 94 g / 59 mL were added in 30 min. The solution was refluxed at  $97 - 100^\circ\text{C}$  for 2h. After cooling to room temperature a nearly colourless, viscous solution is obtained ( $\rightarrow$  TKT 1-94).

The IR spectrum of the material resembles the spectrum of BC 915 with an additional band at  $2726\text{ cm}^{-1}$ .

The Hull cell test (3 A / 5 min.) yields a panel that is bright to semi bright over the whole current density range. The thickness ratio (2.5 cm / 7.5 cm) is determined as  $r = 1.4$  with satisfactory efficiency. A second test was performed at 1 A over 15 min. Here the aspect of the panel was semi bright with stripes in the mcd area. The thickness ratio in this case was determined as  $r = 2.1!!$  The main difference between these two tests is that in the 3 A case a stronger agitation of the bath takes place due to the stronger gas evolution on the cathode. Therefore a Hull cell test was run at 1 A / 15 min with mechanical agitation of the bath. Under these conditions the thickness ratio was found to be  $r = 1.2!$  A comparable strong influence of agitation on the metal distribution had not been observed with any other polymer in the context of this project.

To quantify the influence of the imidazole on aspect and metal distribution the reaction was repeated with a smaller amount of imidazole (ureadmapa / imidazol = 1/10;  $\rightarrow$  TKT 1-98). The efficiency and thickness ratio obtained were comparable to those obtained before. The general brightness was not as good as with the higher imidazole content.

An approach to further improve the properties of the imidazol addition may lie in the use of epichlorohydrin as an additional linking agent. In many cases these product

gave improved brightness and the polarising effect of these products have been proven in the experiments described above.

115 g ureadmapa (0.5 mol) and 6.8 g imidazole (0.1 mol) were dissolved in 210 mL H<sub>2</sub>O and heated to reflux at 98 °C. 70.8 g / 44 mL TMCB were added in 20 min and the mixture was refluxed for 1 h. Afterwards the solution was cooled to 62 °C in 20 min and 15.3 g / 12.9 mL Epi (0.165 mol) were added within 5 min. The mixture was then stirred at 60 °C – 70 °C for 2h. After cooling to room temperature a nearly colourless, viscous solution was obtained (→ TKT 1-101, TKT 1-108)).

The IR spectrum of the material after evaporation of excess water was similar to the one obtained without adding epi but the band at 2726 cm<sup>-1</sup> was missing and some shoulders for the C-OH bands could be seen between 950 and 1150 cm<sup>-1</sup>.

The Hull cell tests performed with this material at different concentrations and different current densities generally yielded panels that were semi bright to bright and showed thickness ratios of  $r = 1.2 - 1.5$ . The current efficiency was found to be somewhat lower than with the TMCB-only polymer but still acceptable.

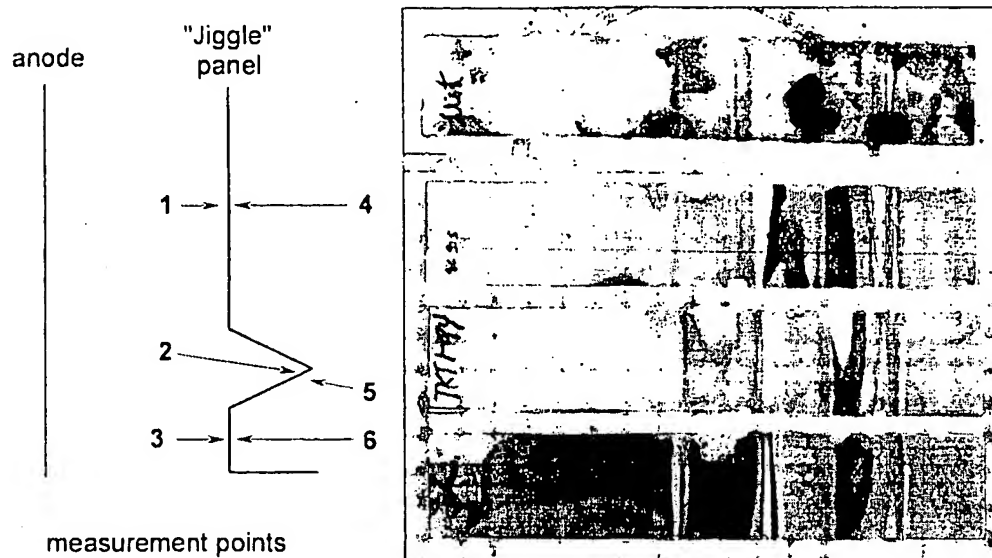
A phenomenon that was encountered with many of the polymers described here should be mentioned at this point. In a variety of cases it was observed that the 3 A panels showed a higher degree of brightness than the 1 A panels. This might be due to the longer plating times which in most cases also yield higher thickness. Nevertheless a certain tendency of these polymers to produce more brightness at higher current densities is observed.

In principle the polymer obtained in this experiment shows very promising properties. A more detailed study could show if this material is of potential use as a brightener additive.

In a comparative test Jiggle cell panels were plated under the following conditions:  
10.5 g/L Zn, 120 g/L NaOH, 10 mL/L 0.2 M Benzyl Pyridinium Carboxylate, 3 A, 30'

- 1) 10 mL/L Mirapol WT (10 %)
- 2) 10 mL/L BC 915 (10 %)
- 3) 10 mL/L TKT 1-94 (12 %)
- 4) 10 mL/L TKT 1-101 (12 %)

The dilutions were chosen to obtain the same concentrations of the polymers in the bath on a weight/volume basis. The panels were flattened after plating and set aside for evaluation of latent blistering.



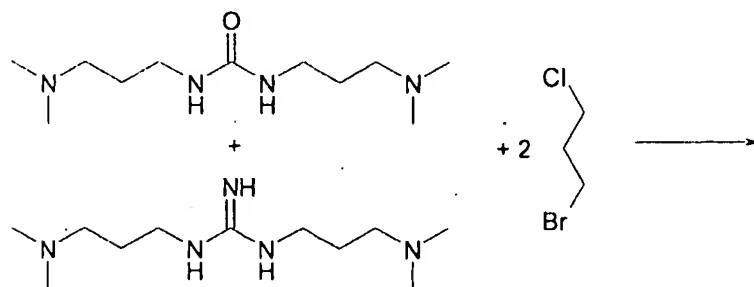
The sketch above shows the position on the panels where the thickness of the deposit was determined by XRF. The picture on the right shows the aspect of the panels when the measurements were taken. The table below shows the thickness measurements taken at these positions and the thickness ratio between the highest and lowest on the front side (3/2) and the highest on the front and the lowest on the back (3/6).

Polymer	1 / $\mu$ in	2 / $\mu$ in	3 / $\mu$ in	4 / $\mu$ in	5 / $\mu$ in	6 / $\mu$ in	3/2	3/6
WT	379	287	384	293	474	299	1.34	1.31
915	324	322	343	299	444	301	1.07	1.15
1-94	433	379	442	365	463	351	1.17	1.26
1-101	335	306	356	175 (?)	438	292	1.17	1.22

The following conclusions can be drawn from this experiment. Concerning the aspect TKT 1-94 was judged to give the best brightness followed by BC 915. Mirapol WT gives the least appealing aspect of the four polymers. Under the given conditions Mirapol WT gives the worst metal distribution while BC 915 gives the best. Both TKT

1-94 and TKT 101 give metal distributions in between but closer to BC 915. It is noteworthy that TKT 1-94 gives the best overall efficiency.

An approach that was mentioned before but had not yet been followed is the co polymerisation of ureadmapa and guanadmapa. This should combine the superior brightness of the guanadin polymers with the superior metal distribution properties of the urea polymers.



In a first experiment 57.5 g ureadmapa (0.25 mol) and 57.3 g guanadmapa (0.25 mol) were dissolved in 195 mL H<sub>2</sub>O and heated to 67 °C. 78.7 g / 49.2 mL TMCB were added within 13 min. and the mixture was refluxed for 2h at 98 – 100 °C. After cooling to room temperature a clear, colourless, viscous liquid was obtained (→ TKT 1-103).

The IR spectrum showed a pattern that could easily be interpreted as a mixture of BC 915 and the guanidin polymer obtained before. E.g. the band at 1643 cm<sup>-1</sup> is much stronger than the one at 1561 cm<sup>-1</sup>, which is due to the presence of the N=C besides the O=C double bond.

The Hull cell test yields a panel that is semi bright to bright. The aspect is more similar to the guanidin product than to BC 915. Also the metal distribution seems to be influenced more by the guanidin function. The thickness ratio at 2.5 and 7.5 cm is determined to be  $r \approx 1.7$ .

Seemingly the properties of this polymer are in all aspects determined mainly by the guanidin function. The reasons for this are not easily understood but a possible approach to overcome this may lie in changing the ratio of ureadmapa and guanadmapa in the polymer.

To verify this a second experiment was performed with a ratio of ureadmapa / guanadmapa = 3 / 1 was performed.



28.6 g guanadmapa (0.125 mol) and 86.3 g ureadmapa (0.375 mol) were dissolved in 195 mL H<sub>2</sub>O and heated to 96 °C. 78.7 g / 49.2 mL TMCB were added within 20 min and the mixture was refluxed at 100 – 103 °C for 3 ½ h. After cooling to room temperature a clear, colourless viscous solution was obtained (→ TKT 1-105).

The IR spectrum of the material was comparable to that of the material obtained with the 1:1 ratio but more similar to BC 915 (as expected).

The Hull cell test yielded panels that were similar in aspect to the ones obtained with the 1:1 ratio. The metal distribution was only slightly improved. The thickness ratio between 2.5 and 7.5 cm depending on the exact conditions was  $r = 1.5 - 1.7$ .

Generally speaking these polymers are not the main candidates for use in zinc and zinc alloy brighteners. The improvement in aspect is traded off directly for a loss of metal distribution. The additional effort of making a further starting material and thus have a three step production (guanadmapa) can not easily be justified by these results.

#### Conclusions:

This study has led to a variety of new insights into the relationship between structures of amine based polymers and their performance as brighteners in alkaline zinc and zinc alloy plating baths. These insights have led to improvements over the commercially available additives.

Several of the polymers synthesised in this study offer advantages over the materials currently in use. This is especially true for the reaction products of ureadmapa with imidazole and trimethylene chlorobromide and the reaction products of ureadmapa with trimethylene chlorobromide and epichlorohydrine. In the tests performed so far they showed a higher degree of brightness and in some cases also a higher current efficiency than Mirapol WT or BC 915. The metal distribution obtainable with the new products is also good.

One of the main advantages of these products is that they are not protected by patents and no prior art has been found that would cover this kind of material.

Therefore it should be considered to apply for a patent that covers the copolymerisation of amines and also the use of epichlorohydrin and other linking agents in one polymer.

Having described the invention, we claim the following:

1. An amine based polymer as described and shown herein.
2. An amine based polymer comprising the reaction product of urea dimethylamino propylamine with trimethylene chlorobromide.
3. An amine based polymer comprising the reaction product of urea dimethylamino propylamine with trimethylene chlorobromide, and epichlorohydrin.
4. An amine base polymer comprising the reaction product of guanidine dimethyl aminopropylamine with trimethylene chlorobromide.
5. An amine based polymer comprising the reaction product of guanidine dimethyl aminopropylamine with trimethylene chlorobromide and epichlorohydrin.
6. An amine based polymer comprising the reaction product of at least one of guanidine dimethyl aminopropylamine and urea dimethylamniopropylamine with at least one of trimethylene chlorobromide and epichlorohydrin.
7. An amine based polymer comprising the reaction product of at least one of guanidine dimethyl aminopropylamine and urea dimethylamniopropylamine with at least one of trimethylene chlorobromide and epichlorohydrin, and with piperazine.
8. An amine based polymer comprising the reaction product of at least one of guanidine dimethyl aminopropylamine and urea dimethylamniopropylamine with at least one of trimethylene chlorobromide and epichlorohydrin, and with imidazole.